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THE RATE OF REACTION BETWEEN FERRIC AND STANNOUS SALTS IN SOLUTION.

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The rate of reaction between ferric and stannous chloride has been investigated by Kahlenberg,¹ Noyes,² Harcourt³ and Timofeew, Muchin and Gurewitsch.⁴ From the six determinations at 0° in varying concentrations of hydrochloric acid by Kahlenberg, the author concluded that the reaction was bimolecular; Kortright,⁵ however, considered that the bimolecular reaction occurred between the hydrolytic products rather than between the ions themselves; Noyes,² on the other hand, found, on recalculating the results that they gave a better trimolecular constant for the more dilute acid solutions, the average deviation from the mean value in one experiment being 8 per cent. Noyes' own experiments showed the effect of variation in the reactant concentrations and in the ratio of iron to tin concentration and of addition of the products of the reaction. Moderately good trimolecular constants were obtained, the variation from the mean value of the constant varying from 3 per cent. to 33 per cent. in different experiments.

Harcourt,³ using another technique, showed that hydrochloric, nitric and phosphoric acid increased the reaction rate, while sulphuric acid was an inhibitor. Timofeew, Muchin and Gurewitsch⁴ were interested in neutral salt effects up to high salt concentration and they also made a few determinations of the temperature coefficient. They appear to have reduced the error to about 3 per cent.

Further investigation was desirable for two reasons. In the first place, although frequent reference is made to neutral solutions, stannous chloride always gives acid solutions by hydrolysis, usually with the formation of a precipitate or turbidity of basic salt which may initiate side reactions in addition to the effect caused by the free acid. Secondly, we have found that the reaction can be followed easily if, in place of the analytical method previously employed, dichromate titration of the ferrous chloride produced in the reaction, the sample is run into a large volume of water containing almost sufficient titanous chloride to reduce the undecomposed ferric chloride and thereupon the reduction is completed by titration in the usual way. With a little experience we were able to perform eighteen titrations in one experiment, yielding "constants" showing an average deviation from the mean of 1.5 per cent. with a maximum deviation of 3 per cent.

¹ *J. Amer. Chem. Soc.*, 1894, 16, 314.

² *Z. physikal. Chem.*, 1895, 16, 546.

³ *Phil. Trans.*, 1913, 212A, 187.

⁴ *Z. physikal. Chem.*, 1925, 115, 161.

⁵ *J. Amer. Chem. Soc.*, 1895, 17, 116.

Experimental.

Ferric chloride solutions were made after chlorinating the salt to remove any traces of ferrous salt. Stannous chloride was made by heating the recrystallised salt in a current of hydrogen chloride, cooling in an evacuated desiccator and dissolution in water to give a solution about 8*M*. This was diluted for use, with hydrochloric acid, to give a solution of the desired acid concentration whose precise value was determined from tin and chloride analyses on each solution.

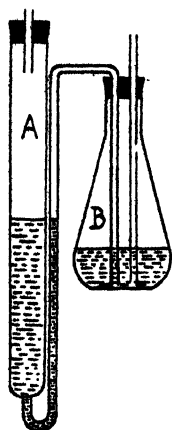


FIG. 1.

Ferric perchlorate was prepared by double decomposition of ferric chloride with the stoichiometric amount of silver perchlorate. Stannous perchlorate was prepared by saturating perchloric acid with stannous hydroxide.

In the reaction experiments the simple apparatus shown in Fig. 1 proved very suitable for the rapid mixing of the reactants essential where the reaction velocity is great, and the transfer and admixture of hot reactants must be carried out without loss of temperature. 100 c.c. of each of the solutions were placed in A and B and forced over from one vessel to the other and back again by repeated alternations of gentle pressure and suction, the whole process taking

less than 40 seconds.

In most experiments the ferric salt concentration was twice that of the stannous salt, in which case the trimolecular constant was calculated from:

$$k_3 = \frac{1}{8a^2t} \cdot \frac{x(2a-x)}{(a-x)^2}$$

where a = initial concentration of stannous chloride,

x = stannous chloride concentration at time t .

In a few cases the iron to tin ratio was 1:1 or 3:1 when the following formulae were used:

$$k_3 = \frac{1}{a^2t} \left[\frac{2x}{a-2x} + \ln \left(\frac{a-2x}{a-x} \right) \right]$$

and

$$k_3 = \frac{1}{a^2t} \left[\ln \left(\frac{3a-2x}{3(a-x)} \right) - \frac{2x}{3(3a-2x)} \right]$$

respectively. Bimolecular constants k_2 were calculated by the usual formula. Table I. gives a selection of data for a run when a good trimolecular constant was obtained:—

TABLE I.

[FeCl₃] = 0.026*M*. [SnCl₂] = 0.013*M*. [HCl] = 0.0185*N*. 25°.

t	= 0	m.s. 1.53	5.8	6.45	9.38	11.13	15.3	23.38	31.40
TiCl ₃ titre in c.c.	= 29.88	27.26	24.58	23.42	21.72	20.82	19.46	16.60	14.98
$\frac{x(2a-x)}{t(a-x)^2}$	= —	(0.107)	0.0931	0.0929	0.0927	0.0945	0.0902	0.0948	0.0940

The following tables summarise our experimental results, velocity constants being expressed with g. mol. per litre and minutes as units, τ being the time of half reaction in minutes. Values of k_1 and k_2 are given in those cases where sufficiently consistent values were obtained to justify mention, τ being the corresponding half period. At moderate acid concentrations the reaction was composite and in these cases τ , obtained from a plot of titre against time, is the better measure of the reaction rate.

TABLE II.—FERRIC CHLORIDE—STANNOUS CHLORIDE REACTION.

Series A. Effect of Acid Concentration at 25°.

[FeCl ₃] = 0.026 M [SnCl ₂] = 0.013 M				[FeCl ₃] = 0.04 M [SnCl ₂] = 0.02 M				[FeCl ₃] = 0.053 M [SnCl ₂] = 0.0265 M				[FeCl ₃] = 0.0826 M [SnCl ₂] = 0.0413 M			
[HCl]	k_1	k_2	τ	[HCl]	k_1	k_2	τ	[HCl]	k_1	k_2	τ	[HCl]	k_1	k_2	τ
0.0088	87.9	—	25.2	0.0090	94.3	—	9.94	0.0099	138.7	3.85	—	0.0186	196	1.12	—
0.0117	79.6	—	27.8	0.0139	83.4	—	11.2	0.0261	156.5	3.43	—	0.0286	220	1.00	—
0.0165	71.0	—	31.2	0.0178	84.8	—	11.1	0.0307	160.2	3.33	—	0.0375	—	0.79	—
0.0170	71.3	—	31.1	0.0227	89.9	—	10.4	0.0351	—	3.25	—	0.0385	—	0.81	—
0.0185	68.8	—	32.2	0.0276	86.7	—	10.8	0.0517	—	2.85	—	0.0414	—	0.80	—
0.0221	65.6	—	33.8	0.0388	92.8	—	10.1	0.0721	—	2.55	—	0.0428	—	0.79	—
0.0480	—	—	32.0	0.0776	—	—	8.0	—	—	—	—	0.0539	—	0.68	—
0.0581	—	—	27.0	0.1032	—	7.3	6.85	—	—	—	—	—	—	—	—
0.0778	—	—	20.3	—	—	—	—	—	—	—	—	—	—	—	—
0.1028	—	5.61	13.8	—	—	—	—	—	—	—	—	—	—	—	—
0.1164	—	6.83	11.3	—	—	—	—	—	—	—	—	—	—	—	—
0.155	—	9.46	8.1	—	—	—	—	—	—	—	—	—	—	—	—
0.181	—	11.0	7.0	—	—	—	—	—	—	—	—	—	—	—	—

Series B. Effect of Varying Fe: Sn Ratio at 25°.

One experiment with a solution [FeCl₃] = 0.0216 M, [SnCl₂] = 0.0216 M, [HCl] = 0.0133 N gave a satisfactory trimolecular constant, k_3 = 99.7.

Series C. Effect of Potassium Chloride at 25°.

[FeCl ₃] = 0.02 M			[SnCl ₂] = 0.01 M			[HCl] = 0.005 N.		
[KCl]	0.0025	0.005	0.005	0.015	0.015	—	—	—
k_3	119.6	124.6	124.6	127.5	127.5	—	—	—

The neutral salt effect is therefore positive even at low concentration.

Series D. Effect of Temperature.

[FeCl ₃] = 0.026 M.				[SnCl ₂] = 0.013 M.				E
[HCl]	15°	20°	25°	30°	30°	30°	30°	
0.0130	k_1 = —	34.2	(73.6)	154.9	—	—	—	26,700
0.0133	k_2 = —	34.4	(73.2)	152.4	—	—	—	26,300
0.0280	k_3 = —	30.2	(61.1)	120.6	—	—	—	24,500
0.0362	k_4 = —	31.8	(63.5)	123.5	—	—	—	24,000
0.0509	τ = —	55.6	(28.8)	15.2	—	—	—	22,900
0.0778	τ = —	—	20.3	11.3	—	—	—	21,000
0.1164	k_5 = 2.03	—	6.83	—	—	—	—	20,700
0.181	k_6 = 3.18	—	11.0	—	—	—	—	21,200

The figures in brackets are interpolated from the Arrhenius formula for comparison with the direct determinations (see Fig. 2a).

TABLE III.—FERRIC PERCHLORATE—STANNOUS PERCHLORATE REACTION.

Series A. Effect of Acid at 50°.

[Fe(ClO ₄) ₃] = 0.0284 M.				[Sn(ClO ₄) ₂] = 0.0142 M.			
[HClO ₄]	0	0	0.0106	0.0211	0.0240	0.0317	0.0611
k_3	231.2	246.0	87.8	57.5	43.9	33.8	7.9
k_4 [H] ²	—	—	0.010	0.026	0.025	0.034	0.030

The addition of 0.02 M KClO₄ to the acid-free solution raised the velocity constant to 250.9.

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Series B. Effect of Variation in Fe: Sn Ratio at 50°.

$[\text{Sn}(\text{ClO}_4)_2]$	0.0158	0.00946	0.0142
$[\text{Fe}(\text{ClO}_4)_3]$	0.0158	0.0284	0.0284
k_3	649	332.4	231.2

Good trimolecular constants were obtained in all three experiments. The lack of agreement between the three values is adequately accounted for by the variation in hydrogen-ion concentration consequent on the different reactant concentrations employed.

Series C. Effect of Temperature.

$[\text{Fe}(\text{ClO}_4)_3]$.	.	0.02	0.0345
$[\text{Sn}(\text{ClO}_4)_2]$.	.	0.01	0.0173
$[\text{HClO}_4]$.	.	0	0
k_3	.	.	$\left\{ \begin{array}{l} 1200 \text{ at } 50^\circ \\ 591 \text{ at } 45^\circ \\ 284 \text{ at } 40^\circ \end{array} \right.$	$\left\{ \begin{array}{l} 275 \text{ at } 55.9^\circ \\ 186 \text{ at } 53.2^\circ \\ 121 \text{ at } 50.0^\circ \end{array} \right.$
E	.	.	29,000 cal.	29,400 cal.

Discussion.

The experimental facts are as follows:

(1) The reaction between the perchlorates gives a good trimolecular constant even up to 0.1 *N* HClO_4 . This is true of the chloride reaction at low acid concentration. Good trimolecular constants are also obtained on varying the ratio of Fe^{+++} : Sn^{++} . However, the trimolecular constants obtained with different concentrations of the acid-free perchlorates are not identical.

(2) Perchloric acid has a powerful retarding effect; to a first approximation

$$[\text{H}^+]^2 \cdot k_3 = 0.029.$$

A similar inhibitory effect is found with low concentrations of hydrochloric acid, although its inhibitory strength is somewhat smaller.

(3) At higher concentrations of hydrochloric acid the velocity passes through a minimum and then increases (see Fig. 2a). The order of reaction is indefinite in the vicinity of the minimum and becomes bimolecular at higher acid concentrations. The acid concentration corresponding to the minimum velocity decreases with increase in concentration of reactant and at the highest concentration employed the minimum occurs at so low an acidity as to be experimentally unrealisable.

(4) Potassium chloride increases the rate of reaction. The effect is of the same magnitude as the effect of acid on the bimolecular constant.

(5) The rate of reaction is greater for the perchlorates than for the chlorides.

(6) The temperature coefficient of the perchlorate reaction corresponds to an energy of activation of 29,200 cal. in neutral solution, while that of the chloride reaction increases with a decrease in acid concentration and extrapolates to a value of about 29,200 cal. in neutral solution (see Fig. 2b).

Equilibrium in mixed solutions of ferric and stannous salts must be complicated by hydrolysis, ionisation in stages and complex formation with acids. The following discussion, therefore, only attempts to deal with the more salient features of the reaction; a full discussion would require a more detailed knowledge of these solutions than is available at present.

It is apparent that at least two reactions are proceeding:

(1) a trimolecular reaction, inhibited by acid and only slightly affected by neutral salts, which predominates at low acid concentration.

(2) a bimolecular reaction accelerated both by acid and neutral salt, important at higher acid concentrations and occurring only with the chlorides.

There are two important facts relating to the first reaction: (a) the inhibitory action of perchloric acid is described by the equation:

$$k_3[\text{H}\cdot]^2 = \text{constant},^*$$

(b) In neutral solution the value of the trimolecular velocity constant is dependent on the concentration of reactants. The relation $k_3[\text{H}\cdot]^2 = \text{constant}$ may be used to calculate the hydrogen-ion concentrations in the acid-free solutions employed as follows:—

$[\text{Fe}(\text{ClO}_4)_3]$.	.	0.02	0.0158	0.0284	0.0284	0.0345
$[\text{Sn}(\text{ClO}_4)_2]$.	.	0.01	0.0158	0.00946	0.0142	0.0173
$[\text{H}\cdot]$.	.	0.0049	0.0053	0.0093	0.0110	0.0155

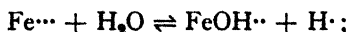
It is difficult to calculate the hydrogen-ion concentration resulting from the hydrolysis of mixtures of ferric and stannous perchlorate, but the calculated values are of the right order and increase with increase of the total reactant concentration, as is to be expected. The figures indicate a total hydrolysis of both salts of 16 to 30 per cent. and make it probable that the apparent divergence between the values of k_3 in acid-free solution is due not to experimental error but to the hydrogen-ion concentration resulting from hydrolysis, which in turn depends on the concentration of reactants.

Fig. 2a shows that the inhibitory effect of hydrochloric acid is somewhat weaker than that of perchloric acid. Moreover, the equation $k_3[\text{H}\cdot]^2 = \text{constant}$ no longer holds so well; this is probably due to the fact that the influence of the second bimolecular reaction is sufficient to accelerate the reaction slightly without appreciably impairing the constancy of the velocity "constant."

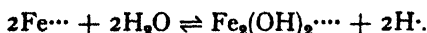
These considerations point to the importance of hydrolysis in this reaction and the true velocity equation seems to be:

$$\frac{dx}{dt} = k'_3 \frac{[\text{FeCl}_3]^2 [\text{SnCl}_2]}{[\text{H}\cdot]^2},$$

where k'_3 is independent of the acid concentration. This opens up two possibilities: (a) the reaction is of the third order between SnCl_2 (or $\text{Sn}\cdot\cdot$) and a hydrolysis product such as $\text{FeOH}\cdot\cdot$ whose concentration is governed by the equilibrium:



(b) the reaction is of the second order between SnCl_2 (or $\text{Sn}\cdot\cdot$) and a polymerised hydrolysis product such as $\text{Fe}_2(\text{OH})_2\cdot\cdot\cdot$ whose concentration is governed by the equilibrium:

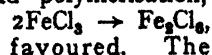


The conductivity measurements of Bjerrum,⁶ however, favour the former possibility. Either mechanism will yield a trimolecular reaction experimentally. The bimolecular reaction between the chlorides at higher acid concentration probably occurs between the tin and a double molecule of Fe_2Cl_6 (or perhaps an ion such as Fe_2Cl_5^+ , etc.). At low acid

* See Table III., Series A; the lack of agreement in the lowest acid concentration is probably due to the fact that, because of hydrolysis, $[\text{HClO}_4]$ is not a correct measure of $[\text{H}\cdot]$.

⁶ *Z. physikal. Chem.*, 1907, 89, 350.

concentrations this reaction will be negligible because most of the ferric salt will be dissociated or hydrolysed, but with an increase in chloride ion concentration ionisation will be repressed and polymerisation,



favoured. The source of the chloride ions, whether acid or salt, should not have a large effect, and in practice it is found that the effect of hydrochloric acid in these experiments is of the same order as that of sodium chloride recorded by Timofeev and his co-workers.⁵ At high acid concentration the titre will be proportional to the concentration of the polymer and this second order reaction will be experimentally bimolecular. At intermediate acid concentrations two reactions will proceed simultaneously, but the kinetics will be complicated. The

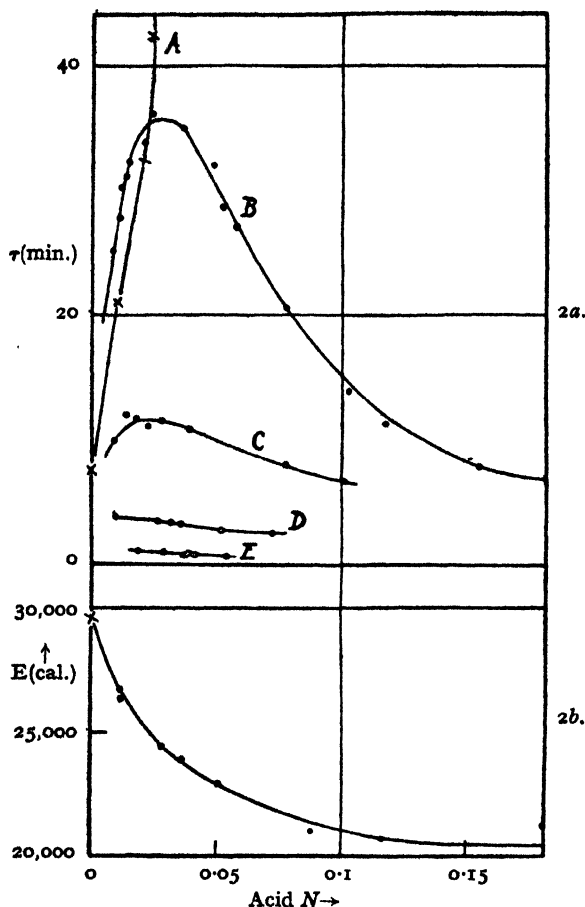
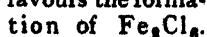


FIG. 2a.—Effect of acid on half period of reaction. Curve A: Effect of perchloric acid on reaction between 0.0284 M $\text{Fe}(\text{ClO}_4)_3$ and 0.0142 M $\text{Sn}(\text{ClO}_4)_2$ at 50°. Curves B, C, D and E: Effect of hydrochloric acid on reaction between FeCl_3 and SnCl_2 at 25°. Curve B. 0.026 M FeCl_3 + 0.013 M SnCl_2 . Curve C. 0.04 M FeCl_3 + 0.02 M SnCl_2 . Curve D. 0.053 M FeCl_3 + 0.0265 M SnCl_2 . Curve E. 0.083 M FeCl_3 + 0.0415 M SnCl_2 .

● Points on Curve B are interpolated from results at other temperatures.

FIG. 2b.—Energy of activation at different acid concentrations. x Point refers to a perchlorate mixture and o points to chloride mixture.

Moreover, it would be anticipated that the influence of the bimolecular reaction would be apparent at a lower acid concentration with increase in reactant concentration, because such an increase would itself favour the



polymerisation and less acid would be required to produce appreciable concentrations of Fe_2Cl_6 .

It was hoped to obtain information from the temperature coefficient, but the apparent energy of activation is too high to account for so fast a reaction.* Consequently the reaction proceeds much more rapidly than would be the case if the energy of activation were 29,200 cal. or alternatively the true energy of activation is, for some reason, much less than the observed. It was at first thought that the rapidity of the reaction could be explained by a hydrolysis increasing with temperature; thus the true velocity constant would be given by:

$$\begin{aligned}\frac{dx}{dt} &= k_{\text{true}}[\text{FeOH}\cdot]^2 [\text{Sn}\cdot\cdot] \\ &= k_{\text{true}}K[\text{FeCl}_3]^2 [\text{Sn}\cdot\cdot],\end{aligned}$$

where K is a factor connecting the hydrolysis product with the total ferric salt concentration. Now if the hydrolysis (and K) increase with temperature, since $k_{\text{obs}} = k_{\text{true}} K$, part of the increase in k_{obs} will be due to an increase in K , i.e., part of the observed energy of activation will be due to a term $RT^2 \frac{d}{dT} \log K$. But Lemoine⁸ has shown that heat is evolved during hydrolysis and therefore hydrolysis diminishes with a rise in temperature. It is, therefore, impossible to account for the reaction on the basis of three-body collisions involving $\text{FeOH}\cdot$ ions.

It is, however, possible that among the hydrolysis products there is a small proportion of $\text{Fe}_2(\text{OH})_2\cdots$ which may be formed endothermically. If this proportion is only 10 per cent., then the number of collisions between $\text{Fe}_2(\text{OH})_2\cdots$ and $\text{Sn}\cdot\cdot$ per c.c. per sec. is 4.2×10^{26} and the true energy of activation would be 14,200 cal. This would necessitate a rapid but not impossible increase in the ratio of $\text{Fe}_2(\text{OH})_2\cdots$ to FeCl_3 with rise in temperature.

At high acid concentrations the energy of activation approaches a value about 21,000 cal. which is also much too large for a bimolecular reaction proceeding at the observed rate. Again the discrepancy is probably due to the neglect of the temperature coefficient of an equilibrium constant, $K = [\text{FeCl}_3]^2/[\text{Fe}_2\text{Cl}_6]$.

Summary.

The reaction between ferric and stannous salts is trimolecular in perchlorate solution due to reaction with a hydrolysis product of the ferric salt; the mechanism may be of the third order but a simple explanation based on a second order mechanism is available. In chloride solution

* From the data of Bjerrum,⁶ a 0.026 M FeCl_3 solution is 23 per cent. hydrolysed, so that $[\text{FeOH}\cdot] = 0.006 M$ (or $[\text{Fe}_2(\text{OH})_2\cdots] = 0.003 M$) and the total number of collisions between $\text{FeOH}\cdot$ and $\text{Sn}\cdot\cdot$ ions is given by the usual formula⁷ as 8.4×10^{27} per c.c. per sec. at 25°. The number of three-body collisions between ($2 \text{ FeOH}\cdot + \text{Sn}\cdot\cdot$) will be much smaller. For acid-free solution at 25° a short extrapolation gives the trimolecular constant as approximately $k_3 = 130$ so that 0.00114 g. molecules of ferric chloride react per litre per min. or 1.15×10^{16} molecules per c.c. per sec. The energy of activation is therefore: $e^{-E/RT} = 1.15 \times 10^{16}/8.4 \times 10^{27}$, whence $E = 16,200$ cal. and even if all the ferric chloride molecules participate in the collisions the energy of activation can be only slightly larger. A mechanism based on three-body collisions must lead to a smaller energy of activation.

⁷ Moelwyn-Hughes, *Kinetics of Reaction in Solution*, 1933, 73.

⁸ *Bull. Soc. Chem.*, 1926, (4), 39, 189.

(with acid or neutral salt) a bimolecular reaction proceeds simultaneously, accelerated by chloride ions, which has been explained by a polymerisation of ferric chloride. Temperature coefficients do not yield the true energies of activation of either reaction because the temperature coefficients of certain equilibrium constants are involved, but it is shown that the assumption of a third order reaction involving hydrolysed ferric ions is incompatible with the observed temperature coefficient. This temperature coefficient, however, is consistent with the assumption that reaction proceeds between one stannous ion and one $\text{Fe}_2(\text{OH})_2^{++}$ ion present in small concentration relative to the total amount of hydrolysed ferric chloride.

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ANOMALOUS DIFFUSION IN TRUE SOLUTION.

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The method generally adopted for measuring diffusion constants is that of Oeholm: a layer of the solution is covered carefully with a layer of the solvent thrice as thick; after a sufficient lapse of time, the whole amount of fluid is divided into four portions, which are analysed. The diffusion constant may then be determined according to Fick's law, from tables calculated by Stefan and Kawalki. In some cases this method gives satisfactory constants, although, even when using small concentrations,¹ other methods fail to do so. Solutions of substances with high molecular weight very frequently deviate strongly from Fick's law,² and do not give constants when investigated by Oeholm's method. A case of this type was first found by Herzog and Polotzky³ in aqueous solutions of dyestuffs. Still more pronounced instances have been detected in solutions of natural products and their derivatives⁴ (cellulose, etc.). There seem to be several possible explanations of these anomalies. That most favoured assumes that the solution is not homogeneous, but contains substances of different molecular weight. Other possibilities are lack of purity, a special chemical reaction with the solvent, the disturbing influence of a structure or of swelling. These explanations had to be discarded in those cases in which similar deviations from Fick's law were found with well-defined substances having a small molecular weight:⁵ quinone diffusing in pure water gives a constant, which

¹ Fürth, *Physik. Z.*, 1925, **26**, 719; Fürth and Ullmann, *Kolloid-Z.*, 1927, **41**, 304; Zuber, *Z. Physik*, 1932, **79**, 291.

² Quite generally. The "diffusion constant" may be a function of the concentration of the diffusing substance or the diffusion may proceed in an anomalous way owing to secondary influences.

³ R. O. Herzog and Polotzky, *Z. physik. Chem.*, 1914, **87**, 449.

⁴ R. O. Herzog and D. Krüger, *J. physik. chem.*, 1929, **33**, 179; R. O. Herzog and Cohn, *Helv. Chim. Act.*, 1928, **11**, 529; v. Frank and Mendrzyk, *Ber.*, 1930, **63**, 875; R. O. Herzog and Kudar, *Z. physik. Chem.*, 1933, **167A**, 343; D. Krüger and H. Grunsky, *ibid.*, 1930, **150**, 115; 1934, **170**, 161; R. O. Herzog, *ibid.*, 1935, **172**, 239.

⁵ H. Freundlich and D. Krüger, *Z. Elektrochem.*, 1930, **36**, 305.

agrees with the value calculated from the molecular weight according to Euler's equation. But if it diffuses in a normal solution of potassium sulphate, for instance, the concentration of the salt being the same in the solution of quinone and in the supernatant layer, Fick's law is not obeyed. This is seen in Tables I. and II. :—

TABLE I.—DIFFUSION OF QUINONE IN PURE WATER.

$h = 2.95$ cm. ; $\tau = 6.94$ days ; $t = 15^\circ$;
 $c = 33.18$ millimols per litre.

No. of Layer.	Amount of Quinone.		$h \left(\frac{\text{cm.}^2}{\text{day}} \right)$.
	Titrated.*	Per Cent.	
I.	0.075	1.05	0.67
II.	0.525	7.35	0.61
III.	2.20	30.6	0.61
IV.	4.375	61.0	0.63
Average value			0.63
Calculated from Euler's equation			0.585

h = height of layer.

τ = duration of diffusion.

t = temperature.

c = initial concentration of the quinone solution.

TABLE II.—DIFFUSION OF QUINONE IN A NORMAL SOLUTION OF K_2SO_4 .

$h = 3.26$ cm. ; $\tau = 6$ days ;
 $t = 11.8^\circ$; $c = 37.45$ millimols per litre.

No. of Layer.	Amount of Quinone.	
	Titrated.	Per Cent.
I.	0.776	9.6
II.	0.833	10.3
III.	2.68	33.1
IV.	3.81	47.0

It is distinctive of this kind of deviation that after a quite short time of diffusion the concentration in the upper layer is much greater than it ought to be. A distribution of the concentration such as in Table II. does not permit calculation of constants from the tables of Stefan and Kawalki. This phenomenon is not due to a wrong distribution of the densities of the liquids from the outset, causing convection currents: the solution containing quinone plus potassium sulphate had a higher density (1.0626) than the upper layer (1.0612). The anomaly was specially pronounced in solutions of sulphates, but it was also very distinct with other salts, such as NaCl, KBr and $NaClO_4$.

Other, as yet unpublished, examples may be mentioned: quinone diffuses normally in solutions of sulphuric acid, although the deviations are so strong in sulphate solutions. Tables III. and IV. record two measurements of this kind, taken from a much greater number.

The method of measurement used in these and the following tables differed from that of Oeholm.* A solution of quinone—solute 1—in an aqueous solution of an electrolyte—solute 2—was carefully allowed to run below a solution containing the same electrolyte, but free of quinone. Both solutions are present in the same amount. A burette containing the aqueous solution of quinone plus electrolyte is mounted on the diffusion cylinder. When taking samples for analysis, the solution in the burette is allowed slowly to displace the liquid in the cylinder. In this way the latter may be subdivided into any number of portions, giving a more intimate knowledge of the distribution of the concentration. In the experiments recorded in Tables III. to IX. the liquid above the median line (33 c.c.) was divided into six layers, one of 8 and five of 5 c.c. The

* C.c. of a 0.1 normal solution of thiosulphate, calculated for 10 c.c. of the layer.

* D. Krüger and H. Grunsky, *loc. cit.*

time of diffusion was the same for "normal" and "anomalous" experiments. The time chosen was so short that in normal experiments the top layer, or even the one below, was practically free of quinone. The difference between normal and anomalous behaviour is most noticeable when the time of diffusion is not too long. The amount of quinone was determined by use of an iodometric method of Valeur.⁷

TABLE III.—DIFFUSION OF QUINONE IN A NORMAL SOLUTION OF H_2SO_4 .

$h = 0.80$ cm.; $\tau = 23$ hours; $t = 18^\circ$;
 $c = 59.2$ millimols per litre.

Layer	Amount of Quinone.	
	Titrated.*	Per Cent.
33-25	0.025 (one drop)	< 0.4
25-20	0.050 (two drops)	< 0.8
20-15	0.10	1.7
15-10	0.40	6.7
10-5	1.10	18.6
5-0 †	2.30	38.8
0-5	3.85	65.0
5-10	5.00	84.5
10-15	5.83	98.4

TABLE IV.—DIFFUSION OF QUINONE IN A 1-NORMAL SOLUTION OF Na_2SO_4 .

$h = 0.80$ cm.; $\tau = 23$ hours;
 $t = 18^\circ$; $c = 57.5$ millimols per litre.

Layer.	Amount of Quinone.	
	Titrated.	Per Cent.
33-25	0.235	4.1
25-20	0.30	5.2
20-15	0.50	8.7
15-10	0.90	15.7
10-5	1.55	27.0
5-0	2.70	47.0
0-5	3.625	63.1
4-10	4.725	82.4
10-15	5.00	87.0

The calculation is not so simple as when using Oeholm's method (*cf.* Krüger and Grunsky).⁶ The diffusion constant may be determined from an equation derived by Boltzmann, if the column of liquid is considered as practically infinite in both directions, and provided that so many layers are analysed that a region of constant concentration is reached. In the experiments recorded in Tables III. to XI., the conditions for calculating the constant were not very favourable: the analysis of the layers was not always extended far enough; the height of the layers was not known sufficiently exactly, and the time of diffusion was too short. The chief aim was merely to show the difference in distribution of the diffusing substance in normal and anomalous diffusion.

It should be mentioned that the percentages in the Tables III. to IX. have not the same meaning as in the Tables I. and II. The total volume and the total amount of the diffusing substance are not known, when using the method of Krüger and Grunsky, as is the case when applying the method of Oeholm. Therefore the percentages in the Tables III. to IX. refer to fractions of the original concentration of the diffusing substance, not to fractions of the total amount.

The anomalous diffusion is evidenced, not solely by extraordinarily high concentrations in the upper layers, but, curiously enough, also by a much steeper slope of the concentration of the diffusing substance near

* C.c. of a 0.1-normal solution of thiosulphate, calculated for 5 c.c. of the layer. This also applies to Tables IV.-IX.

† The line in Tables III.-IX. is meant to indicate the original position of the medium line.

⁷ Valeur, *C.r.*, 1899, 129, 552.

the median line. This behaviour is shown by Fig. 1: the abscissæ are the layers, the ordinates the concentrations; the continuous curve corresponds to the case of normal diffusion, the dotted one to that of anomalous diffusion.

Mr. G. S. Hartley, when discussing the possible causes of anomalous diffusion, pointed out to us that we might perhaps be dealing with a case of what Thover called "*diffusion rétrograde*," owing to which an inadmissible distribution of densities might arise, once diffusion had begun. This might cause disturbance by convection currents, which could be avoided so long as the upper layer had a distinctly lower concentration of salt than the solution containing the diffusing substance.

This explanation is well founded. The anomalous diffusion may really be deduced from papers by Thover⁸ and G. S. Hartley⁹ on the diffusion and distribution in a solvent of graded composition.

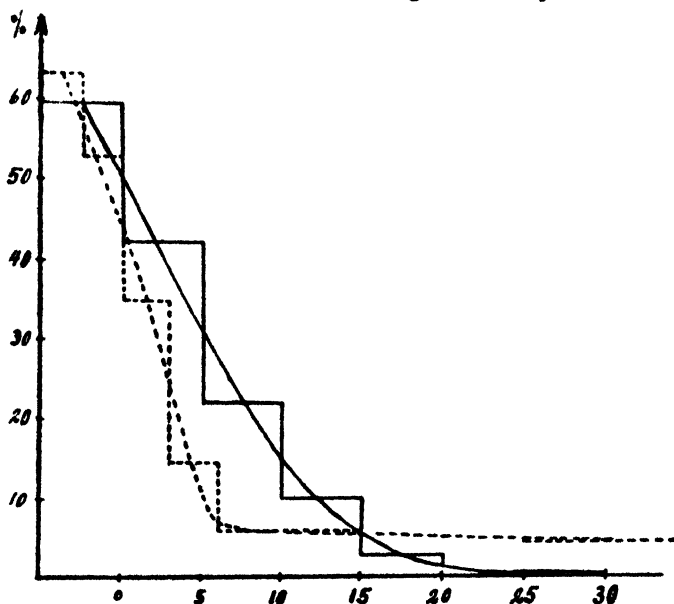


FIG. 1.

— quinone in water.

---- quinone in 90 per cent. acetic acid.

A solute, originally in uniform distribution in a liquid column, may be made to diffuse, if a gradient of a suitable force is kept up in the column. The best-known case of this kind is the so-called Soret effect: if a temperature gradient is maintained in a column of a solution having originally the same concentration throughout, a difference in concentration is produced between the hotter and the cooler regions. This is not merely due to the change in osmotic pressure,¹⁰ caused by the different temperatures, as was assumed by van't Hoff. The difference in solubility¹¹

⁸ Thover, *Ann. physique*, 1914, (9), 2, 369.

⁹ G. S. Hartley, *Trans. Farad. Soc.*, 1931, 27, 10.

¹⁰ G. S. Hartley, *ibid.*, 1931, 27, 1.

¹¹ The term "solubility" is meant to imply all those forces not due to osmotic pressure, i.e., the forces active in "salting out" or caused by changes of the internal pressure of the liquid, indicated in changes of compressibility, surface tension, etc.

caused by the change of temperature is also important, i.e., we are dealing not only with a movement of the molecules of the solute, but also of the solvent and of any other matter present, and these movements produce a stationary state depending not only upon the osmotic pressure but also upon the forces governing solubility.

According to Hartley, the following case is theoretically even simpler. A solution of a solute 2 of uniform concentration may be expected to show a change in its distribution, provided that, at constant temperature, a concentration gradient is maintained between two parts of the liquid, for instance, owing to the presence of a solute 1 in one part of the solution. The forces of which the gradients are active in this case are those which solute 1 exerts upon solute 2, when changing the solubility of the latter.

As mentioned above, cases of this kind were first observed by Thovert, who offered no explanation of them, and did not emphasise the importance of an interaction between the two solutes, which is made noticeable by a change of solubility. Thovert was investigating the influence of one diffusing electrolyte upon a second electrolyte, the latter being from the outset in uniform concentration, an effect which might be foreseen from the point of view of the dissociation theory. But the effects observed did not agree with the theoretical deductions; moreover, dissociation proved to be not at all essential to this phenomenon: a uniformly distributed electrolyte (NaCl) could be made to diffuse by an unequally distributed non-electrolyte (alcohol or sugar), or, again, both solutes 1 and 2 could be non-electrolytes (alcohol and sugar or vice versa).

The conditions of some of the cases investigated by Thovert agree fully with those of our experiments: he found, for instance, that NaCl, originally distributed uniformly, shows a definite change in concentration, determined by analysis, if an organic substance (alcohol or sugar) was present in unequal distribution and was therefore diffusing in the liquid column. In our case, the change in concentration of the electrolyte is made evident in an indirect way: owing to its diffusion, the correct distribution of densities prevailing originally is not maintained; a thin

TABLE V.—DIFFUSION OF QUINONE
DISSOLVED IN A NORMAL Na_2SO_4
SOLUTION INTO A 0.75-N. Na_2SO_4
SOLUTION.

$h = 0.80$ cm.; $\tau = 23$ hours;
 $t = 18^\circ$; $c = 59.5$ millimols per litre.

Layer.	Amount of Quinone.	
	Titrated.	Per Cent.
33-25	0.025 (1 drop)	< 0.4
25-20	0.025 (1 drop)	< 0.4
20-15	0.15	2.5
15-10	0.47	7.9
10-5	1.16	19.5
5-0	2.30	38.6
0.5	3.60	60.5
5-10	4.76	79.9
10-15	5.35	89.9
15-20	5.70	95.6

TABLE VI.—DIFFUSION OF
QUINONE IN 78 PER CENT.
ACETIC ACID.

$h = 0.80$ cm.; $\tau = 23$
hours; $t = 21^\circ$; $c = 91.0$
millimols per litre.

Layer.	Amount of Quinone.	
	Titrated.	Per Cent.
33-25	0.33	3.6
25-20	0.335	3.7
20-15	0.345	3.8
15-10	0.41	4.5
10-5	0.95	10.4
5-0	2.38	26.1

layer of liquid close to the median line may become less dense than the liquid above; convection currents are set up and disturb the regular trend of the diffusion of the quinone.

It is probable that this decrease in density will not exceed a certain limit; the whole disturbance may therefore be avoided, if only the electrolyte solution above is to a sufficient degree less dense. The following experiments prove this assumption to be correct.

Table V. records an experiment where the quinone is dissolved in a normal solution of Na_2SO_4 , but this solution is covered with a 0.75 *N*. solution of the same salt. When comparing this table with Table IV., it is evident that the distribution of the diffusing substance is now normal. Even more cogent are the following experiments with acetic acid. Solutions of this substance in water have a maximum of density at about 80 per cent. acetic acid. Quinone, diffusing in a solution having a concentration of 78 per cent. of acetic acid throughout, shows an anomalous behaviour (Table VI.). But if it is dissolved in a solution of about the same strength (79.5 per cent.) and this solution is covered with a more dilute one (45.5 per cent., Table VII.), or a more concentrated one (glacial acetic acid, Table VIII.), the anomalies disappear.

TABLE VII.—DIFFUSION OF QUINONE DISSOLVED IN 79.5 PER CENT. ACETIC ACID INTO A 45.5 PER CENT ACETIC ACID.

$h = 80$ cm.; $\tau = 23$ hours; $t = 23^\circ$; $c = 97.0$ millimols per litre.

Layer.	Amount of Quinone.	
	Titrated.	Per Cent.
33-25	0.021 (1 drop)	< 0.2
25-20	0.034 (1 drop)	< 0.35
20-15	0.10 (3 drops)	< 1.0
15-10	0.45	4.6
10-5	1.55	16.0
5-0	3.65	37.6

TABLE VIII.—DIFFUSION OF QUINONE DISSOLVED IN 79.5 PER CENT. ACETIC ACID INTO GLACIAL ACETIC ACID.

$h = 0.80$ cm.; $\tau = 23$ hours; $t = 23^\circ$; $c = 87.0$ millimols per litre.

Layer.	Amount of Quinone.	
	Titrated.	Per Cent.
33-25	0.047 (2 drops)	0.5
25-20	0.085 (3 drops)	about 1
20-15	0.25	2.9
15-10	0.75	8.6
10-5	1.825	21.0
5-0	3.525	40.6
0-5	5.625	64.7

One may conclude from these results that, if an anomalous diffusion occurs, the two solutes present interact, mutually changing their solubility, thus causing a diffusion of the uniformly distributed solute 2 and, in consequence, an anomalous density gradient and convection currents in the neighbourhood of the border line. If diffusion is normal, also in presence of a second solute—for instance in cases of quinone in solutions of sulphuric acid or glucose in solutions ⁵ of NaNO_3 —this may be due to the fact that the change in solubility, caused by the other solute is insufficient to bring about a diffusion of solute 2. It is, however, certainly not impossible that there are other cases of the latter kind, where, notwithstanding the fact that the solubility is changed, the rapid diffusion of solute 1, and other factors, may cancel any disturbance due to the change in solubility.

Anomalous diffusion is distinctly different from intertraction,¹² a phenomenon also caused by convection currents due to an inadmissible distribution of densities. In cases of intertraction the solute, the diffusion of which causes the disturbance, is not present in uniform concentration from the outset. There are two different solutes diffusing in opposite directions, and if the rates of diffusion are very different, it may happen that a heavier layer is formed above a lighter one. Intertraction may cause further macroscopically visible changes, and the liquid is fairly soon thoroughly mixed up. This does not occur in cases of anomalous diffusion; if it did, the latter would not be so well reproducible as they are. It is specially remarkable from this point of view that the slope of concentration near the original border line retains its original steepness, while diffusion proceeds. Table IX. proves this assertion: quinone was

TABLE IX.—DIFFUSION OF QUINONE IN 90 PER CENT. ACETIC ACID.

$h = 0.80$ cm.; $t = 19^\circ$; $c = 84.6$ millimols per litre.

Layer.	Amount of Quinone Titrated.		Layer.	Amount of Quinone Titrated, $\tau = 21.75$ Hours.
	After $\tau = 3.5$ Hours.	$\tau = 7.75$ Hours.		
33-25	0.070 (2 drops)	0.20	33-25	0.46
25-20	0.075 (2 drops)	0.25	25-20	0.50
20-15	0.075 (2 drops)	0.25	20-15	0.50
15-10	0.075 (2 drops)	0.315	15-10	0.53
10-5	0.25	0.375	10-6	0.53
5-0		2.425	6-3	1.25
			3-0	3.00
			0-2.5	4.50
			2.5-5	5.40

allowed to diffuse in an uniformly distributed solution of acetic acid (90 per cent.) in three parallel experiments; the layers were analysed at different times τ .

Although this behaviour is not in every way compatible with the conception of convection

currents, in a rough sense of the word, the experiments recorded in Tables V., VII., and VIII. seem to show definitely that anomalous diffusion may be made to disappear, if only great care be taken to avoid an inadmissible distribution of densities.

Summary.

Anomalies of diffusion, such as are found, for instance, when quinone is diffusing in aqueous solutions of electrolytes, may be explained as follows: the existence of a concentration gradient (of the quinone) in the aqueous solution from the outset may cause the uniformly distributed substance also to diffuse, owing to a mutual change in solubility of the two solutes (G. S. Hartley). In consequence, in the course of the diffusion process, a thin layer of the liquid on the border line of the two solutions may become less dense than the solution above, and this inadmissible density gradient may produce convection currents disturbing the normal process of diffusion. The correctness of this assumption was proved by the fact that the anomalies

¹² A. E. Wright, *Proc. Roy. Soc.*, 1921, 92B, 118; *ibid.*, 1926, 112A, 212; 1927, 114, 576; 1929, 125, 587; Schooneboom, *ibid.*, 1922, 101A, 531; Peskoff, *Kolloid-Z.*, 1923, 33, 215; Szegvari, *ibid.*, 1923, 33, 324; N. K. Adam and Jessop, *Proc. Roy. Soc.*, 1925, 108A, 324; N. K. Adam, *ibid.*, 1926, 113A, 478; *Kolloid-Z.*, 1931, 56, 138.

disappeared when care was taken that the solution above was to a sufficiently marked degree less dense than the one below.

We would like to thank Mr. G. S. Hartley very sincerely for his most suggestive advice.

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THE VOLUME COEFFICIENT OF EXPANSION OF DEUTERIUM.

By J. B. M. COPPOCK, PH.D.

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Urey and Teal¹ after a careful examination of the physical properties of hydrogen and deuterium conclude that their P - V - T relations may be represented by an equation of state common to both gases. This view is supported by experimental data here obtained from a direct comparison of the coefficients of expansion at constant pressure of hydrogen and deuterium over the same temperature interval and at almost identical pressures. The mean value found for deuterium is about one part in six thousand less than that assigned to hydrogen: such a difference is within the limits of experimental error. It may be concluded therefore that the coefficients at constant pressure and constant volume for the two isotopes are identical.

Experimental.

The gases were prepared by decomposition of water vapour by passage over reduced iron (carbon free) at 600° C.,² undecomposed water vapour was frozen out in three successive liquid air traps, and the gases finally dried over P_2O_5 .

The modified Callendar Thermometer used for the comparison of the expansion coefficients of the two isotopes has been previously described by Coppock and Whytlaw-Gray.³ The only difference in procedure was that in the present work the thermometer was used to indicate two fixed points approximately at 11° C. and 48° C. The weight of mercury w removed from the Callendar Thermometer in order to restore equality of pressure on changing the temperature from the lower to the higher value (through T° C.) was determined for standard hydrogen. This was then replaced by deuterium and determinations made with the heavy isotope over the same temperature interval. Assuming the appropriate expansion coefficients of hydrogen the exact value of T was calculated, and from a knowledge of this the expansion coefficient of deuterium obtained.

A silica expansion vessel was used, the volume of gas V contained at t° C. = 158.73 c.c. and the coefficient of cubical expansion β of the vessel, which included a silica to glass seal, = 0.0000020. The results have been calculated from the following equations:—

$$\alpha = \frac{\alpha_1}{1 - \alpha_1 T}, \quad . \quad . \quad . \quad . \quad (1)$$

$$\alpha_1 = \frac{wf + V\beta T}{T[V - wf]}, \quad . \quad . \quad . \quad . \quad (2)$$

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where $t^{\circ}\text{C.}$ = initial temperature of the gas and the temperature of the mercury removed (11.08°C.).

f = conversion factor gms. mercury to c.c.s. at $t^{\circ}\text{C.}$

α_t = volume coefficient of expansion of the gas from $t^{\circ}\text{C.}$ to $(t + T)^{\circ}\text{C.}$

α = volume coefficient of expansion of the gas when referred to the volume of gas at 0°C.

Results.

Three determinations were made with each gas, the accuracy claimed should not be less than one part in four thousand. The deuterium was about 98 per cent. pure; no correction for the presence of 2 per cent. light hydrogen need be applied to the results.

VALUES OF w FOR THE TWO ISOTOPES OVER THE SAME TEMPERATURE RANGE.

Gas.	$t^{\circ}\text{C.}$	Pressure in mm.	w in gms.	Mean w .
Hydrogen . . .	11.08	693	248.162	248.136
	11.08	693	248.137	
	11.08	693	248.109	
Deuterium . . .	11.08	690	248.087	248.097
	11.08	690	248.095	
	11.08	690	248.108	

The value assumed for the volume expansion coefficient of hydrogen has been obtained from the data of Henning and Heuse ⁴ and Heuse and Otto.⁵ Interpolation of their results gives the mean value of $10^6\alpha^{0-100}$ at 693 mm. = 3659.6. It has been previously shown ³ that values obtained over the range 11.48°C. when corrected to the volume of the gas at 0°C. , are identical with determinations made over the range $0-60^{\circ}\text{C.}$ The correction to be applied to α^{0-100} to give α^{0-60} has been calculated from a modification of the Beattie-Bridgeman equation of state⁶; introduction of this correction gives $10^6\alpha^{0-60} = 3659.7$. Insertion of this value in equations (1) and (2) gives $T = 37.048^{\circ}\text{C.}$ Assuming this quantity the value obtained for deuterium is $10^6\alpha^{0-60} = 3659.1$ at 690 mm. pressure, and inserting the correction for change of α with temperature it is found that $10^6\alpha^{0-100} = 3659.0$.

The author wishes to express appreciation of the encouragement and facilities given him by Dr. J. Kenyon and Professor R. Whytlaw-Gray, F.R.S., who kindly supplied him with a sample of pure water.

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- ¹ Urey and Teal, *Review of Modern Physics*, 1935, 7, 34.
- ² Hinshelwood, Williamson, Wolfenden, *P.R.S.*, 1934, A 147, 48.
- ³ Coppock and Whytlaw-Gray, *P.R.S.*, 1934, A 143, 487.
- ⁴ Henning and Heuse, *Z. Physik*, v. and vi., 1921, pp. 285, 264.
- ⁵ Heuse and Otto, *Ann. Physik*, 1929, 2, 1012.
- ⁶ Coppock, *J. Physic. Chem.*, 1933, 37, 995.

THE ISOELECTRIC POINT OF ISINGLASS.

BY H. FREUNDLICH AND P. S. GORDON.

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1.

Isinglass is a protein prepared from the swimming bladder of the sturgeon (or in inferior qualities from other fish such as the dog fish). It strongly resembles gelatin and is widely used in commerce, for instance in the "clearing" of beer, where freshly brewed beer is "cleared" by the addition of a small amount of isinglass solution. The properties of isinglass have scarcely been investigated at all, except for some experiments by Zsigmondy¹ on its protective action upon gold sols. We intend to fill this gap. This paper will mainly deal with the isoelectric point of isinglass solutions.

The following method of preparation was used. The dried swimming bladder was cut into thin strips which were soaked in several changes of distilled water until nearly all the salts had been removed. This took 2 to 3 days. The isinglass was then brought into solution by heating with distilled water to 70° to 75° for a period of 15 to 20 minutes, with constant stirring. The cloudy solution so obtained was filtered through glass wool and allowed to cool, then the gel was dried over CaCl_2 in a vacuum desiccator. The product so obtained was a horny, transparent, sheet with a slight yellow colour.

This preparation is quite unlike that used in breweries, where the isinglass is brought into solution by swelling with sulphurous acid and calcium bisulphate; but such a method of preparation was felt to be unsuitable on account of the large amounts of salts introduced.

2.

The isoelectric point was determined by a micro-cataphoretic method. The migration of the protein was not investigated directly, but, instead, the cataphoretic velocity of quartz particles coated with a sufficiently thick layer of isinglass was measured. It has been shown² that the cataphoresis of particles covered with a protein depends upon the pH in exactly the same way as does the cataphoresis of the protein molecules in aqueous buffer solution. At the isoelectric point neither the protein coated particles nor the protein molecules migrate. The cataphoretic velocity of the particles was determined by a microscopic method.

Details of this method have been described in the papers just mentioned.

The apparatus (see Fig. 1) was constructed of Jena glass. The electrodes were



FIG. 1.

of Cu, and were surrounded by a CuSO_4 -agar gel. This was found to be satisfactorily reversible. The electrodes were separated from the tube

¹ Zsigmondy, *Z. analyt. Chem.*, 1901, 40, 697.

² H. Freundlich and H. A. Abramson, *Z. physik. Chem.*, 1928, 133, 51; H. A. Abramson, *J. Amer. Chem. Soc.*, 1928, 50, 390.

by membranes of parchment paper. It was found that these membranes were not quite impermeable to Cu-ions. These ions become so firmly adsorbed by the glass walls of the cell that ordinary washing does not remove them; they can, however, be removed by filling the cell with a CaCl_2 solution, followed by repeated washing with distilled water. Further the cell was completely dismantled at intervals and cleaned with a mixture of sodium dichromate and concentrated H_2SO_4 . These precautions exclude any disturbance, caused by impurities coming from the walls, on particles moving in their neighbourhood.

The solutions of proteins used for the measurements contained about 10^{-3} to 10^{-2} gms./litre, while the buffers used were $M/200$ acetate buffers. (With buffers of higher concentration the heat dissipated in the cell by the passage of the current was found to cause uncontrollable streaming). The p_H was determined with the quinhydrone electrode. The size of the quartz particles was about 1 to 5μ .

Having filled the cell it was used in a horizontal position on a microscope with an eyepiece scale (calibrated by an object scale). In using the apparatus a steady P.D. was maintained between the electrodes by a potentiometer across 220 volt D.C. mains. The P.D. was measured by an accurate, high resistance, voltmeter.

Measurements of the particle velocity were taken at different levels in the cell. These velocities were found to lie on a parabolic curve, in agreement with the formula of Smoluchowski. If v is the velocity of electro-osmotic flow at a distance x from the side of a cavity of width d , and if v_0 is the velocity near to the wall, Smoluchowski showed that

$$v = v_0 \left[1 - 6 \left\{ \frac{x}{d} - \left(\frac{x}{d} \right)^2 \right\} \right].$$

From this it will be seen that the true cataphoretic velocity is only found approximately when

$$\frac{x}{d} = 0.2 \text{ or } 0.8.$$

The velocities found are shown in Fig. 2. It must be mentioned that the temperature was not controlled during the experiments. The extreme range was between 10° and 14° , but the majority of the measurements were taken at a temperature of 12° .

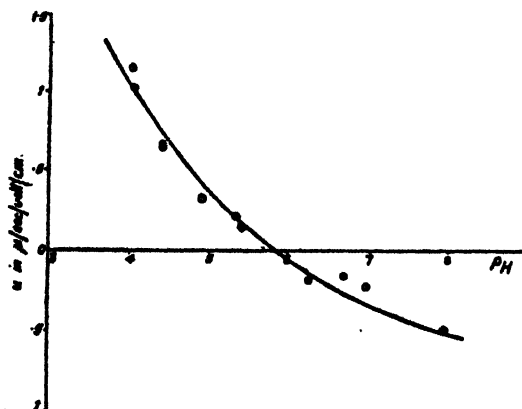


FIG. 2.

It will be seen that a reasonably good curve is obtained, and that the graph is curved over its whole length. At the isoelectric point the cataphoretic velocity is zero, i.e., where the curve cuts the axis for p_H . This is at the p_H of 5.9; the probable error does not seem to be greater than about ± 0.1 , and there-

fore the isoelectric point can be said to lie between 5.8 and 6.0.

3.

Now it was felt desirable to confirm this value by an independent method. A simple method of doing so is offered by a measurement of

the sedimentation volume of particles (again for instance of quartz) coated with the protein. It has been found by Lindau² that the sedimentation volume under these conditions generally has a maximum at the isoelectric point. This is due to the following facts: provided that hydration is not markedly dependent upon a change in p_H , the sedimentation volume is strongly influenced by the electric charge of the particles. As long as they are charged, they only have a slight tendency to aggregate, on the contrary they glide on each other and thus assume a fairly close packing. But uncharged, *i.e.*, at the isoelectric point, the protein coated particles are apt to form loose aggregates which enclose a large amount of liquid and thus cause a maximum sedimentation volume.

A quantity of quartz particles (acid purified sand) was ground in a ball mill till the particles had a diameter of about 1 to 10 μ . Particles outside this range were removed by sedimentation in water. In calculating the required time of sedimentation Stokes' formula was used, assuming the particles to be spherical; this is not strictly true, but the error is of no account here. Before use the quartz was well cleaned by boiling with dilute aqua regia.

Fixed amounts of quartz powder were shaken with buffer solutions of various p_H containing the same amount of isinglass. These experiments were carried out in a series of pyrex test tubes of about 1 cm. diameter and 30 cm. length; care was taken to select tubes of equal cross section; 30 c.c. of each of a series of *M*/50 acetate buffer solutions of graded p_H values were placed in the tubes with a few c.c. (2-4) of an isinglass solution. The tubes were closed by a rubber bung and strongly shaken. After settling for a few hours the depth of the sediment was measured.

The tubes were then again shaken and the sedimentation again measured. This gave the rather curious result that in every case the volume was less than the previous value. As it seemed possible that the effect might be due to the presence of air, experiments were performed in which the quartz settled with the tube evacuated. It was found that as the tube was evacuated bubbles of gas, evidently of air, rose in a constant stream. After the quartz had been allowed to sediment several times in this way the volume reached a steady value. In Table I. experiments of this kind are recorded.

TABLE I.—2 GMS. OF QUARTZ POWDER + 2 C.C.S 1 PER CENT. ISINGLASS SOLUTION (CONCENTRATION OF THE SOLUTION AFTER MIXING WITH THE BUFFER 0.0625 PER CENT.).

p_H Value.	4.4.	4.9.	5.3.	6.0.	6.2.
Volume of sedimentation .	1.5	2.2	2.25	2.7	2.5
On settling <i>in vacuo</i> . .	0.8	1.15	1.35	1.7	1.5
On resettling <i>in vacuo</i> . .	0.8	1.1	1.1	1.4	1.2

The same effect is found in absence of the protein, but it is not so large (see Table II).

² H. Freundlich and G. Lindau, *Biochem. Z.*, 1931, **234**, 170.

TABLE II.—2 GMS. OF QUARTZ POWDER; 30 C.C.S OF A $M/20$ ACETATE BUFFER OF $p_H = 4.95$.

Volume of sedimentation	1.67
On settling <i>in vacuo</i>	1.50
On resettling <i>in vacuo</i>	1.46
On resettling <i>in vacuo</i>	1.45

TABLE III.—2 GMS. QUARTZ POWDER + 25 C.C.S ACETATE BUFFER OF $p_H = 4.95 + 2$ C.C.S 1 PER CENT. ISINGLASS SOLUTION.

Volume of sedimentation	4.67
On settling <i>in vacuo</i>	3.48
After shaking	3.50
After reshaking	3.70

The effect is not reversible: if the system is shaken again with air after a smaller value of the sedimentation volume had been reached on evacuation, only a small increase of volume occurs, the higher original value is not obtained (see Table III.).

We are obviously dealing with the same phenomenon as that described by Spring,⁴ when he investigated the sedimentation volume of powders, specially of a fine sand, in air and *in vacuo* and also in presence of liquids. His results led him to believe that each grain of sand was covered with a layer of air. But it seems doubtful, whether this layer is to be considered entirely or to a marked extent as an adsorbed film; the lack of reversibility and the great thickness of the layer—the amount of air removed by evacuation would correspond to a film three molecules thick—do not agree with this assumption. It is more probable that fine bubbles of air remain sticking to the grains of the powder, because the surface of the particles is not wetted sufficiently quickly and thoroughly. We cannot as yet give a conclusive reason why the amount of air released is larger when isinglass is present. It may be due to a difference in the velocity of wetting or the wettability; but it may also be correlated to the fact that protein solutions have a higher solubility for air and other gases and a stronger tendency to favour supersaturation.⁵

Table I. shows that the correlation between the maximum of the sedimentation volume and the isoelectric point is maintained independently of the influence of air upon the absolute value of the former. The maximum lies at a p_H of about 5.8 to 6.0. The same result was obtained in a second similar series of experiments, where, all other conditions being the same, 3 c.c. of a 1 per cent. isinglass solution had been added (concentration of the solution after mixing with the buffer 0.091 per cent.). The value of the isoelectric point determined in this way agrees well with the one derived from the cataphoretic measurements.

4.

Some further experiments were performed to confirm the correlation between maximum of sedimentation volume and isoelectric point and, more particularly to see whether the influence of air is found to the same extent in other cases. Freundlich and Lindau³ have carried out their measurements with gelatin and egg albumen. These experiments were repeated with practically the same results: the maximum was found at the isoelectric point, 4.9 for gelatin and 4.5 for a carefully electrodyalysed egg albumen.—The values of Freundlich and Lindau were 4.9 for gelatin and 4.6 to 4.7 for egg albumen.—The influence of air was also very distinct: in the case of gelatin in a buffer of 4.9 the

⁴ Spring, *Bull. Soc. Belg. Géol.*, 1903, 17, Mém. 13.

⁵ Cf. A. Findlay and Th. Williams, *J. Chem. Soc.*, 1913, 103, 636; A. Findlay and G. King, *ibid.*, 1913, 103, 1170; 1914, 105, 1297; A. Findlay and O. R. Howell, *ibid.*, 1922, 121, 1046.

sedimentation volume changed from 2.7 to 1.5 on evacuation, in that of egg albumen of the same p_H from 1.25 to 1.1. The influence of air seems to diminish on the alkaline side; with gelatin for instance there was practically no change on evacuation at a $p_H = 6.2$.

The following experiments with electro dialysed hæmoglobin show that also in the case of a protein with a very different value of the isoelectric point the correlation with the maximum of sedimentation volume is maintained.

TABLE IV.—2 GMS. OF QUARTZ POWDER + 4 C.C.S OF 1.9 PER CENT. HÆMOGLOBIN SOLUTION (CONCENTRATION OF THE SOLUTION AFTER MIXING WITH THE BUFFER 0.224 PER CENT.).

p_H Value.	5.4.	6.1.	6.7.	7.8.	9.0.
Volume of sedimentation .	1.2	1.3	1.3	1.2	1.1
On settling <i>in vacuo</i> . .	1.0	1.0	1.2	1.0	0.9

In this case the influence of the air was not so great as in those mentioned above.

Summary.

1. The isoelectric point of isinglass in aqueous solution was found to be 5.9, when measuring by a microscopic method the cataphoretic velocity of quartz particles, coated with isinglass, in buffer solutions.
2. The sedimentation volume of quartz particles in buffer solutions containing isinglass showed a maximum at 5.8 to 6.0, thus confirming the correlation between maximum of sedimentation volume and isoelectric point found in solutions of other proteins.
3. In the experiments in (2) the absolute value of the sedimentation volume was strongly dependent on the presence of air; it might decrease to half its value on evacuation. In absence of isinglass this decrease was smaller, as a rule about 10 per cent. This effect is not reversible: if the evacuated system, having a small sedimentation volume, is shaken with air, the volume only increases slightly without attaining the original high value.
4. The main results in (2) and (3) were confirmed with other proteins such as gelatin, egg albumen and hæmoglobin.

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THIXOTROPY, INFLUENCED BY THE ORIENTATION OF ANISOMETRIC PARTICLES IN SOLS AND SUSPENSIONS.

BY H. FREUNDLICH AND F. JULIUSBURGER.

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When investigating the thixotropy of sols with strongly anisometric, *i.e.* rod- and plate-like particles, one of us (F. J.) observed a surprising influence exerted by the orientation of the particles on the rate of solidification.

The following experiment may serve as example: an aqueous paste of gypsum powder, containing 42 per cent. by weight of gypsum (2 gm. of gypsum, the diameter of the particles being about $1\text{--}10\mu$, and 2.75 c.c. of water) was distinctly thixotropic. After being liquefied by strong shaking, it solidified, if left to itself in a test tube of 1 cm. diameter, in about 40 minutes. If the tube containing this sample, liquefied again by strong shaking, was rolled slowly to and fro between the palms of the hands, thus causing a circular movement of the liquid, it solidified in 20 seconds.—Foam which sometimes forms on the surface of the mass must be carefully destroyed by tapping the tube, otherwise the effect sought may be difficult to perceive.

This experiment may be repeated at will: the strongly shaken system remains liquid for quite a long time, but solidifies rapidly, if the liquid is given a regular movement.

There seems to be no doubt that this movement causes an orientation of the particles; the regularity of the stirring applied inhibits movements in a vertical axis, and rod-shaped particles are therefore oriented entirely with their axes lying horizontally. This becomes evident, if sols of V_2O_5 are investigated. The sol used was about 10 years old; it contained 0.19 per cent. V_2O_5 ; the particles are pronouncedly rod-shaped, as is proved by the beautiful streaks appearing, when the sol is stirred, and by its strong stream double refraction. The sol was made thixotropic¹ by adding 2 drops of 2 N. H_2SO_4 solution (0.1 c.c.) to 4 c.c. of the sol. After violent shaking it solidified in about 60 minutes. The liquid rolled in the fashion mentioned above solidified in about 15 seconds. If this process of rapid solidification is investigated in reflected light, one sees the whole liquid becoming filled up with beautiful annular striations, *i.e.*, the particles are oriented in horizontal zones. If a strongly shaken V_2O_5 -sol is tested by letting the liquid flow gently up and down the test tube, it becomes to a certain degree gelatinous, even after the first flow, evidently because this gentle movement is sufficient to cause orientation.²

We are here dealing with cases in which systems with strongly anisometric particles show differing properties according to the manner in which the particles are arranged. When orienting the particles regularly, *e.g.*, parallel to each other, solidification seems to take place instantaneously; on the other hand a much longer time is necessary to cause spontaneous solidification of the sol, owing again to some kind of struc-

¹ Freundlich and Miss Schalek, *Z. physik. Chem.*, 1924, 108, 153; Jochims, *Kolloid-Ztschr.*, 1927, 41, 215; Rabinerson, *ibid.*, 1934, 68, 305. The thixotropic V_2O_5 -sol containing H_2SO_4 is not very stable.

² Presumably orientation by other forces, for instance by a magnetic field, will also cause a similar rapid solidification.

ture, which may differ markedly from the regular one arising from gentle movement. The annular structure visible in the case of the V_2O_5 -sol shows that the gel solidified by orientation is different from the one formed slowly in the course of time.

When compared superficially there is a certain similarity between this new phenomenon and dilatancy.³ Dilatancy is the effect shown by mixtures of particles with a certain amount of liquid, where the mass turns harder and drier on dislocating the particles, but becomes softer and moister, when the external force ceases to act. Owing to the dislocation of the particles the interstices are enlarged; the system is able to enclose more liquid and therefore appears drier and harder. This point of similarity—solidification by movement—should not be overrated, for, in the case of dilatancy, the new state produced by the dislocation of the particles is not in a state of equilibrium; on the contrary, the material returns to the original, more liquid state, as soon as the external force stops acting. The state of a thixotropic gel solidified by orientation is, on the other hand, one of equilibrium; the material does not turn liquid again, when left to itself.

Although colloid science is overcrowded with new technical terms, it seems inevitable that systems of this kind should be characterised by a special name; it is too cumbersome to say "thixotropic sols which can be solidified by orienting the particles." Graham⁴ used the word "pectous"—derived from "*πηκτός*, solidified, curdled"—for sols which have turned to a jelly. We therefore propose to call a thixotropic sol, which may be solidified by gentle movement, "rheopectic," and the phenomenon itself "rheopexy."⁵

So far we have been unable to discover rheopexy in the well-known thixotropic sols of Fe_2O_3 and Al_2O_3 , containing small amounts of electrolytes, nor in bentonite suspensions. We are specially interested in the behaviour of myosin sols which we hope soon to be able to test. This globulin found in muscles forms thixotropic aqueous sols which are strongly stream double refracting;⁶ its particles are obviously pronouncedly anisometric. It may therefore be expected to show rheopexy. Should this be the case, then rheopectic behaviour might play a certain part in the action of muscles.

Summary.

Thixotropic sols (for instance those of V_2O_5) or suspensions (for instance gypsum + water) containing anisometric particles solidify rapidly, in the course of a few seconds, as soon as the particles are oriented by a gentle movement. The same systems need a much longer time, up to an hour, to solidify spontaneously.

We are much indebted to the Central British Fund for German Jewry for a personal grant to one of us (F. J.). We also wish to thank Mr. A. D. Jones for experimental help.

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³ Osborne Reynolds, *Phil. Mag.*, 1885, (5), 20, 469; *Nature*, 1886, 33, 429.

⁴ Th. Graham, *Phil. Trans. Roy. Soc.*, 1861, 151, 184.

⁵ Rheopexy will most likely make itself felt in the anomalous viscosity of sols with anisometric particles; their viscosity may therefore be even more complicated than was suggested by W. Kuhn, *Kolloid-Z.*, 1933, 62, 269.

⁶ v. Muralet and Edsall, *Trans. Faraday Soc.*, 1930, 26, 837.

THE DISSOCIATION CONSTANTS OF SOME POLYBASIC ACIDS.

BY W. R. MAXWELL AND J. R. PARTINGTON.

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The present communication deals with the acids formed by substituting hydrogen atoms in benzene by carboxyl groups :

$C_6H_5(COOH)$ Benzoic Acid	$C_6H_4(COOH)_2[1 : 2]$ Phthalic Acid	$C_6H_4(COOH)_2[1 : 3]$ Iso-Phthalic Acid
$C_6H_3(COOH)_3[1 : 2 : 3]$ Hemi-Mellitic Acid	$C_6H(COOH)_5$ Benzene Pentacarboxylic Acid	$C_6(COOH)_6$ Mellitic Acid

It is hoped to discuss the remaining members of this series in a later paper. The primary object was a further examination of the effect on the dissociation caused by the presence in the molecule or ion of one or more $-COOH$ or $-COO^-$ groups. This continues previous work concerned with dibasic acids.¹ The method used to determine the dissociation constants was again that of electrometric titration. For the purpose of calculating the dissociation constants of acids of basicity higher than three, an extension of the existing theory was necessary and is described.

Experimental.

Preparation of Acids and other Materials.

Benzoic Acid (B.D.H.) was recrystallised five times from conductivity water. M.-pt., 121.5° .

Phthalic Acid (B.D.H.) was recrystallised five times from conductivity water.

Iso-phthalic Acid (B.D.H.) was recrystallised twice from a large amount of conductivity water (2 gm. *iso*-phthalic acid in 1 litre of boiling water). M.-pt., 345.5° .

Hemi-mellitic Acid.—1 : 8-naphthalene-dicarboxylic acid prepared by oxidising acenaphthene with sodium dichromate and glacial acetic acid,² was oxidised to phenylglyoxyldicarboxylic acid with alkaline permanganate and then to hemi-mellitic acid with weakly acid permanganate.³ The acid was isolated as the acid potassium salt, $C_6H_2(COOH)_3 \cdot COOK$, which by treatment with ammonia and barium chloride was converted into the sparingly soluble barium salt, and the latter was decomposed with the calculated quantity of dilute sulphuric acid. The acid was recrystallised five times from conductivity water. Water of crystallisation was removed by heating at $100-110^\circ C$. in a vacuum over phosphorus pentoxide. M.-pt., 196.5° .

Benzene Pentacarboxylic Acid.—This was prepared by the oxidation of pentamethyl benzene with neutral permanganate.⁴ The pentamethyl benzene was prepared by the methylation of xylene by the Friedel-Craft's

¹ Ashton and Partington, *Trans. Faraday Soc.*, 1934, **30**, 598.

² Graebe and Gfeller, *Ber.*, 1892, **25**, 652.

³ Graebe and Leonhardt, *Lieb. Ann.*, 1895, **290**, 218.

⁴ Friedel and Crafts, *Ann. Chim. Physique*, [6], **1**, 473.

reaction as described by Smith and Dobrovolny.⁵ According to these authors, a good yield of hexamethyl benzene cannot be obtained by the direct methylation of xylene, whilst actually it was found that about 50 per cent. of the product was hexamethyl benzene and absorption of methyl chloride was still taking place. The products, after decomposition in the usual manner, were repeatedly fractionated in a vacuum and consisted mainly of penta- and hexa-methyl benzenes. Final purification was effected by recrystallising twice from alcohol and a mixture of alcohol and chloroform respectively. In the oxidation, 15 gm. of pentamethyl benzene (M.-pt., 51°) were allowed to stand for five months with 75 gm. KMnO_4 and 300 c.c. water in a loosely corked flask which was occasionally shaken. The acid was obtained through the silver salt and was recrystallised from nitric acid of Sp. G. 1.3-1.4, freed from adhering nitric acid by heating at 160° in a vacuum over caustic potash for eight hours, and ultimately recrystallised from about 50 c.c. of hot water. The snow-white needles after dehydration in a vacuum melted at 237°.

Mellitic Acid.—6 gm. of hexamethyl benzene (M.-pt., 161-162°) were oxidised with 36 gm. KMnO_4 in 180 c.c. of water for three months.⁶ Mellitic acid was obtained through the silver salt, was recrystallised from 140 c.c. of nitric acid, Sp. G. 1.3-1.4, and freed from adhering acid as described above. The product was snow-white, sintered in air at 160°, and its approximate M.-pt. in sealed tubes determined by the plunge method was 285°. The absence of appreciable quantities of nitrate was confirmed.

A check on the purity of the acids was obtained from the end-points in the actual titrations. The acids were dried in a vacuum over phosphorus pentoxide for several days before weighing out.

Caustic Soda.—This was prepared by the action of water vapour on metallic sodium,⁶ and was stored in an 8-litre bottle coated with paraffin wax which had been boiled several times with distilled water to remove electrolytes. The bottle was fitted with an outlet tube coated on the inside with paraffin wax and an inlet tube carrying potash and soda lime tubes. The strength was found by titration with hydrochloric acid and methyl red buffered to a p_H of 5.2, except in the case of solutions weaker than 0.01N which were made up by accurate volumetric dilution.

The conductivity water was obtained from a Bousfield still.

Method.

The method and apparatus were the same as described by Ashton and Partington,¹ except that the solid plugs in the titration vessel were replaced by finely ground hollow plugs as shown in Fig. 1. These allowed the bridge to be filled very readily, the procedure being to insert the plugs tightly and then, by means of a pipette drawn out to a fine point, to introduce saturated KCl solution to a level slightly higher than the maximum level attained by the liquid in the titration vessel. The junction is formed at the top of the closed plug and there is a slight hydrostatic pressure tending to cause a flow of KCl solution from the bridge to the titration compartment. This flow was negligibly small. As in previous determinations, liquid junction potentials were neglected, but some justification for doing this was attempted. A cell having three separate bridges, each fitted in the middle with a greased stopcock, was used. The bridges were filled with KCl solutions of different concentrations and E.M.F. measurements were made with each bridge in turn. With a solution of benzoic acid of p_H about 3, the E.M.F.'s with a saturated (4N) and a half-saturated KCl

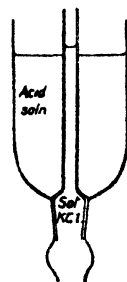


FIG. 1.

⁵ Smith and Dobrovolny, *J. Amer. Chem. Soc.*, 1926, 48, 1413.

⁶ Findlay, "Practical Physical Chemistry," fourth edition, p. 173.

bridge were the same, but with 0.1*N* KCl the E.M.F. was about 2 millivolts less. Thus, it would seem that with saturated KCl as a bridge solution liquid junction potentials could be neglected. The standard electrode was the 0.1*N* calomel, the standard potential of which was taken as 0.3334 volt at 25°. The calomel was prepared by electrolysis, and pure KCl and mercury were used. The electrode vessels were of the type used by Lewis, Brighton, and Sebastian,⁷ but having a three-way T-stopcock to enable fresh calomel electrode solution to be run through the side arm, in place of two separate stopcocks. A tube containing calomel electrode solution was fitted over the connecting tube of the electrode when not in use. This type of electrode has a very constant and reproducible potential, an electrode which had been used for nine months differing in potential from a freshly made one by not more than 0.03 m.v. The quinhydrone used was B.D.H. quality, and was found satisfactory without further purification. If the standard potential of the quinhydrone electrode is taken as 0.7175 - 0.00074*t*, (*t* = °C.) then at 25°:

$$p a_H = \frac{0.3656 - E}{0.05915},$$

where *E* is the measured E.M.F. All titrations were carried out at 25° in an air thermostat, the temperature of a liquid in which was constant to ± 0.2°. The E.M.F.'s were measured by means of a two-dial thermoelectric potentiometer (H. Tinsley & Co.) giving E.M.F.'s directly to four places of decimals. The Weston cell used was checked periodically against an N.P.L. standard. The leads to the potentiometer were screened and the system of shielding advocated by White⁸ was adopted. The apparatus was checked by measurements with Walpole's acetate buffers. All titrations made were repeated and potentials could readily be reproduced to within 0.2-0.3 m.v. except in the immediate neighbourhood of the end-point and during the last third of the titration at the lowest concentrations of benzene pentacarboxylic and mellitic acids.

Calculation of Results.

Morton⁹ has deduced the following equation for the titration of a tribasic acid with a monoacid base:

$$\frac{k_1 a_H^2 / f_1 + 2k_1 k_2 a_H / f_2 + 3k_1 k_2 k_3 / f_3}{a_H^3 + k_1 a_H^2 / f_1 + k_1 k_2 a_H / f_2 + k_1 k_2 k_3 / f_3} = \frac{\omega}{C_a} \quad (1)$$

where *C_a* = the total concentration of acid and its salts;

ω = concentration of metal ions + concentration of hydrogen ions - concentration of hydroxyl ions;

*f*₁, *f*₂, etc., are the activity coefficients of the acid anions;

*k*₁, *k*₂, etc., are the thermodynamic dissociation constants.

An extension of Morton's theory (using accepted notation) for an *n*-basic acid gives the equation:

$$\frac{k_1! \cdot a_H^{n-1} / f_1 + 2k_2! \cdot a_H^{n-2} / f_2 + 3k_3! \cdot a_H^{n-3} / f_3 + \dots + nk_n! / f_n}{a_H^n + k_1! \cdot a_H^{n-1} / f_1 + k_2! \cdot a_H^{n-2} / f_2 + k_3! \cdot a_H^{n-3} / f_3 + \dots + k_n! / f_n} = \frac{\omega}{C_a},$$

where *k_n*! is the product *k*₁ · *k*₂ · *k*₃ · . . . *k_n*.

By cross multiplication it is seen that:

$$\begin{aligned} -\omega a_H^n + a_H^{n-1} \frac{(C_a - \omega)}{f_1} \cdot k_1! + a_H^{n-2} \frac{(2C_a - \omega)}{f_2} \cdot k_2! \\ + \dots + \frac{(nC_a - \omega)}{f_n} \cdot k_n! = 0 \quad (2) \end{aligned}$$

⁷ Lewis, Brighton and Sebastian, *J. Amer. Chem. Soc.*, 1917, **39**, 2244.

⁸ White, *J. Amer. Chem. Soc.*, 1914, **36**, 2011.

⁹ Morton, *Trans. Faraday Soc.*, 1928, **24**, 14.

By putting

$$-\omega a_{\text{H}}^n = u, \quad a_{\text{H}}^{n-1} \cdot \frac{(C_{\alpha} - \omega)}{f_1} = a_1, \quad a_{\text{H}}^{n-2} \cdot \frac{(2C_{\alpha} - \omega)}{f_2} = a_2,$$

and so on, and taking n different points on the titration curve it is found that:

$$\frac{k_r!}{k_{r-1}!} = k_r = \frac{\begin{vmatrix} a_{11}, a_{21}, \dots, a_{(r-1)1}, u_1, a_{(r+1)1}, \dots, a_{n1} \\ a_{12}, a_{22}, \dots, a_{(r-1)2}, u_2, a_{(r+1)2}, \dots, a_{n2} \\ \vdots \\ a_{1n}, a_{2n}, \dots, a_{(r-1)n}, u_n, a_{(r+1)n}, \dots, a_{nn} \end{vmatrix}}{\begin{vmatrix} a_{11}, a_{21}, \dots, a_{(r-2)1}, u_1, a_{r1}, \dots, a_{n1} \\ a_{12}, a_{22}, \dots, a_{(r-2)2}, u_2, a_{r2}, \dots, a_{n2} \\ \vdots \\ a_{1n}, a_{2n}, \dots, a_{(r-2)n}, u_n, a_{rn}, \dots, a_{nn} \end{vmatrix}} \quad (3)$$

Thus, for example, k_2 for a tribasic acid is given by:

$$k_2 = -\frac{u_1(a_{12} \cdot a_{33} - a_{13} \cdot a_{32}) - u_2(a_{11} \cdot a_{33} - a_{13} \cdot a_{31}) + u_3(a_{11} \cdot a_{32} - a_{12} \cdot a_{31})}{u_1(a_{22} \cdot a_{33} - a_{23} \cdot a_{32}) - u_2(a_{21} \cdot a_{33} - a_{23} \cdot a_{31}) + u_3(a_{21} \cdot a_{32} - a_{22} \cdot a_{31})}$$

Morton's equation for k_2 as printed is incorrect, and should read:

$$k_2 = \frac{(\Delta_1\phi_2 - \Delta_2\phi_1)(\phi_1\psi_3 - \psi_1\phi_3) - (\Delta_1\phi_3 - \Delta_3\phi_1)(\phi_1\psi_2 - \phi_2\psi_1)}{(\theta_1\phi_3 - \theta_3\phi_1)(\phi_1\psi_2 - \phi_2\psi_1) - (\theta_1\phi_2 - \theta_2\phi_1)(\phi_1\psi_3 - \phi_3\psi_1)}$$

The correct formula was apparently used in the actual calculations. For pentabasic and hexabasic acids the equations become too large to be practicable, and methods of successive approximation are necessary. k_1 is obtained by neglecting all terms after the $k_3!$ term in (2) and solving for k_1 as in the case of a tribasic acid. The three points most conveniently chosen are one from each of the first three regions of the curve. k_2 is calculated by using three points, one from each of the second, third, and fourth regions of the curve and the equation obtained by neglecting terms above the $k_4!$ term in equation (2). Since $k_1!$ is known, however,

$-\omega a_{\text{H}}^n + a_{\text{H}}^{n-1} \frac{(C_{\alpha} - \omega)}{f_1} \cdot k_1!$ is put equal to u . When $k_2!$ is found a similar procedure is adopted for $k_3!$, terms above the $k_5!$ term being neglected in (2) and u is equated to

$$-\omega a_{\text{H}}^n + a_{\text{H}}^{n-1} \frac{(C_{\alpha} - \omega)}{f_1} \cdot k_1! + a_{\text{H}}^{n-2} \frac{(2C_{\alpha} - \omega)}{f_2} \cdot k_2!$$

In the case of a pentabasic acid, the remaining constants are readily found from expressions derived from (2). For a hexabasic acid

$$-\omega a_{\text{H}}^6 + a_{\text{H}}^5 \frac{(C_{\alpha} - \omega)}{f_1} \cdot k_1! + a_{\text{H}}^4 \frac{(2C_{\alpha} - \omega)}{f_2} \cdot k_2! + a_{\text{H}}^3 \frac{(3C_{\alpha} - \omega)}{f_3} \cdot k_3!$$

is equated to u and the same procedure is used to find $k_4!$, $k_5!$, and $k_6!$. More accurate values for $k_1!$, etc., may now be found, e.g., by putting:

$$-\omega a_{\text{H}}^6 + a_{\text{H}}^5 \frac{(4C_{\alpha} - \omega)}{f_4} \cdot k_4! + a_{\text{H}}^4 \frac{(5C_{\alpha} - \omega)}{f_5} \cdot k_5! + \frac{(6C_{\alpha} - \omega)}{f_6} \cdot k_6! = u.$$

In the above equations ω is equal to $C_{\beta} + h - K_w/h$, where C_{β} is the concentration of the Na ion, h the concentration of the hydrogen ion,

and K_w the ionic product of water. In all cases K_w/h was negligibly small. The hydrion activity coefficient was obtained from the equation of Bjerrum and Unmack:¹⁰

$$-\log f_H = 0.504\sqrt{\mu} - 1.64\mu \quad \text{at } 25^\circ \text{C.} \quad (4)$$

and μ was obtained from the expression given by Söderbäck¹¹ (oh can be neglected):

$$\mu = \omega \cdot \frac{\left[\frac{K_1}{a_H} + \frac{3K_1K_2}{a_H^2} + \dots + \frac{n+n^2}{2} \cdot \frac{K_n!}{a_H^n} \right]}{\left[\frac{K_1}{a_H} + \frac{2K_1K_2}{a_H^2} + \dots + n \cdot \frac{K_n!}{a_H^n} \right]} \quad (5)$$

where K_1, K_2 , etc., are the "imperfect" dissociation constants. In the case of phthalic acid, which has two constants of greatly differing magnitude, the expression $\mu = \omega$ was used in the first region, and $\mu = 2\omega - C_a$ in the second.¹¹ In (5) approximate values of K_1, K_2 , etc., were obtained by putting $h = a_H$, and ω was equated to $C_\beta + a_H$ as a first approximation. In the case of benzene pentacarboxylic and mellitic acids, only the first three or four constants were used in expression (5).

The Activity Coefficients, f_1, f_2 , etc.

Brönsted's simplified form of the Debye-Hückel equation gives the relation between a thermodynamic dissociation constant k_r and the corresponding "imperfect" dissociation constant K_r :

$$\begin{aligned} pk_r &= pK_r + A[r^2 - (r-1)^2]\sqrt{\mu} - (\beta_r - \beta_{r-1})\mu \\ &= pK_r + A[2r-1]\sqrt{\mu} - (\beta_r - \beta_{r-1})\mu. \end{aligned}$$

Thus, if K_r is known for various values of μ , $(\beta_r - \beta_{r-1})$ and hence a value for pk_r are obtained by plotting $pK_r + A(2r-1)\sqrt{\mu}$ against μ . Since K_r is calculated from n different points each at a different ionic strength, and each point has a different influence on the value of K_r , it is in general impossible to state at what ionic strength K_r has been calculated. When the successive constants of an acid differ considerably in order of magnitude, however, the point in the region corresponding to the constant dominates the calculation, so that the constant so found refers to an ionic strength corresponding to this point. The following method, which is free from any assumption, was tried in the case of phthalic acid and could be extended to acids of higher basicity. Equation (1), by cross-multiplication and rearrangement, gives:

$$k_1 \cdot a_H \cdot \frac{(C_a - \omega)}{f_1} + k_1 k_2 \frac{(2C_a - \omega)}{f_2} = \omega a_H^2 \quad (6)$$

C_a and ω are plotted against pa_H , and the point of intersection of the lines corresponds with $C_a = \omega$. The value of pa_H for this point can be read off and equation (6) in logarithmic form reduces to

$$\log k_1 k_2 - \log f_2 = 2 \log a_H.$$

Let

$$-\log f_2 = 4A\sqrt{\mu} - \beta_2\mu,$$

then

$$4A\sqrt{\mu} - 2 \log a_H = \beta_2\mu - \log k_1 \cdot k_2 \quad (7)$$

¹⁰ Bjerrum and Unmack, *Kgl. Danske Videnskab. Selskab.*, 1929, 9, 73.

¹¹ Söderbäck, *Arkiv. Kemi, Mineral Geol.*, 1933, 11A, 1-48.

For two or more titrations at different concentrations, β_2 and $\log k_1 k_2$ can thus be obtained by plotting the left-hand side of (7) against μ .

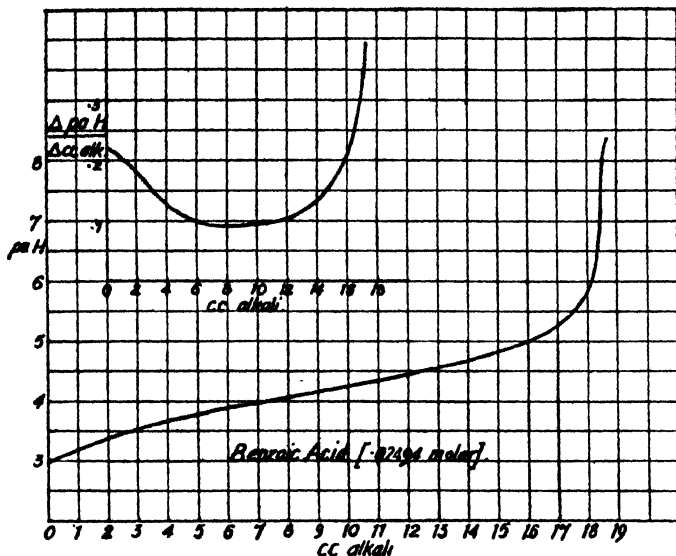


FIG. 2.

The value of $k_1 k_2 / f_2$ is then found at any point on the titration curve and inserted into equation (6), so that k_1 / f_1 can be determined at different

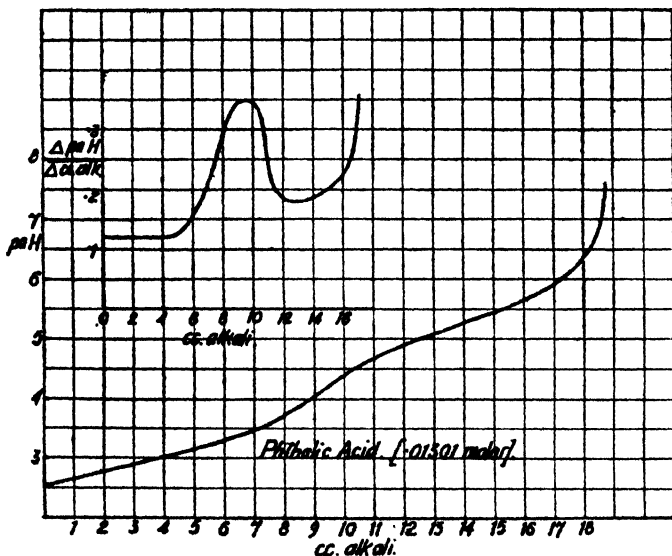


FIG. 3.

ionic strengths, and hence k_1 can be found by a method similar to that used for k_1 , k_2 , and k_3 is then obtained. This procedure applied to phthalic acid showed that (7) did not even approximately represent a

straight line, *i.e.*, the Debye-Hückel theory could not be assumed to hold at the concentrations used. The activity coefficients were therefore necessarily neglected and the imperfect constants calculated.

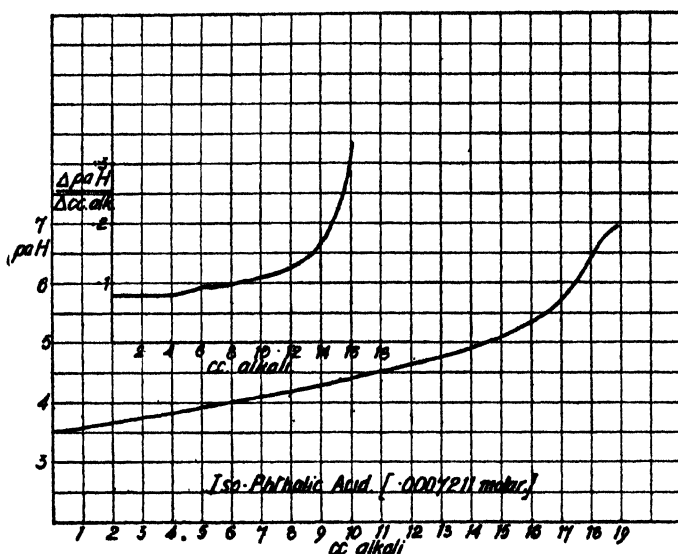


FIG. 4.

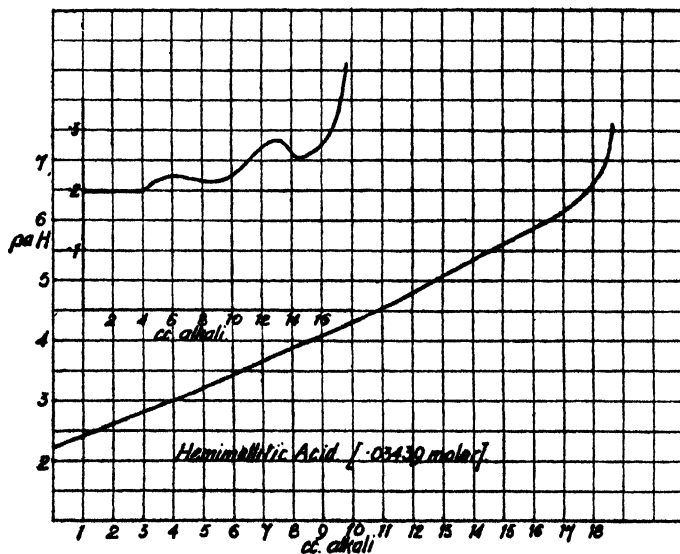


FIG. 5.

Remarks on the Titrations.

The curves obtained by plotting pH against c.c. alkali show in general a number of more or less definite changes of direction, this number being equal to the basicity of the acid. This is more apparent on plotting

$\Delta p a_H / \Delta$ c.c. alkali against c.c. alkali, as shown in the inset graphs. In the case of benzene pentacarboxylic acid only four "humps" are observed (Figs. 2 to 7).

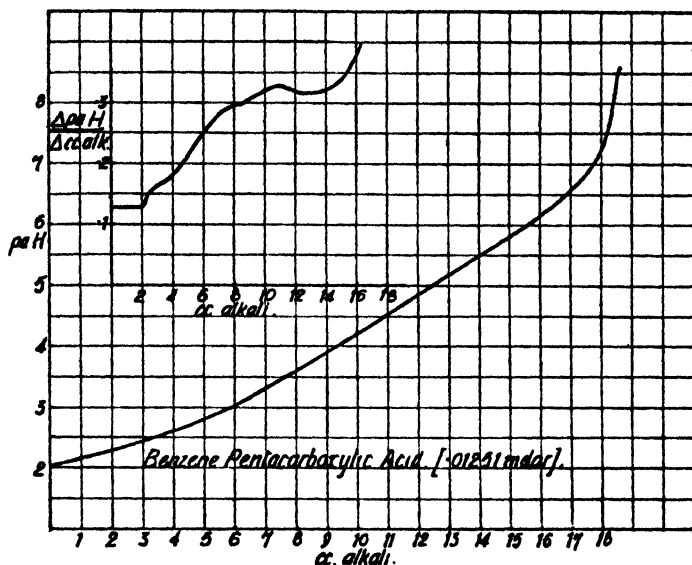


FIG. 6.

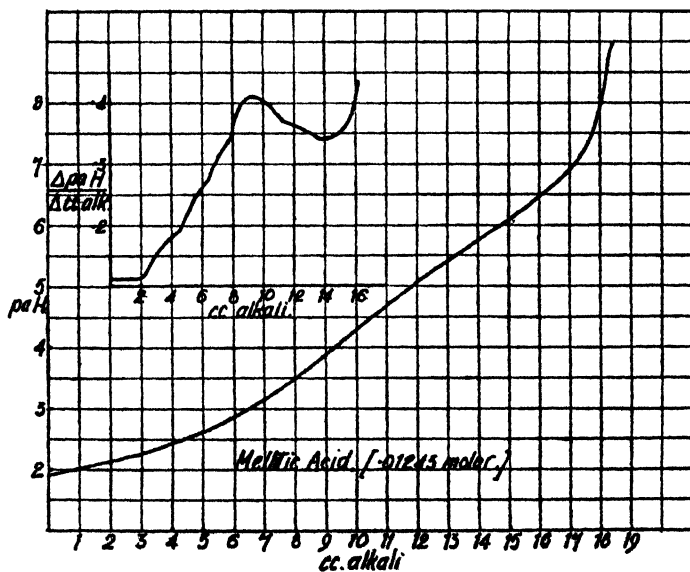


FIG. 7.

In the case of benzoic acid the electrometric end-point, although almost the same as the theoretical end-point when titrating a 0.025*N* solution of the acid, was about 1 per cent. too high in the case of a 0.01*N* solution. This displacement of the electrometric end-point has been observed in

the case of other acids,¹² and points in the neighbourhood of the end-point were therefore avoided as much as possible in the calculation of the constants. It was also noticed in the case of the simpler acids, especially benzoic acid, that if the point corresponding to 0 c.c. of alkali was used in the calculation of K_1 the value of the latter was considerably smaller than that obtained by using other points. The values of the constants calculated for the acids measured at the various concentrations used are given in Table I. (I-16), and the data necessary for their calculation in Table II. (I. to XVI.). The volume of acid solution used for each titration was 20.05 c.c.

TABLE I.

Benzoic Acid (1).—(Acid = 0.02494 molar; alkali = 0.02711 molar.)

<i>c.c. alkali</i>	0.00	2.00	4.02	6.03	8.03	10.00	12.02	14.01	16.02
$k \times 10^6$	5.11	5.89	6.13	6.28	6.41	6.50	6.46	6.57	6.48

Benzoic Acid (2).—(Acid = 0.02023 molar; alkali = 0.02211 molar.)

<i>c.c. alkali</i>	0.00	1.99	4.00	6.03	8.01	10.02	12.00	14.03	16.00
$k \times 10^6$	5.04	5.85	6.14	6.20	6.31	6.39	6.54	6.63	6.59

Benzoic Acid (3).—(Acid = 0.01011 molar; alkali = 0.01105 molar.).

<i>c.c. alkali</i>	0.00	2.00	4.02	6.02	8.02	10.00	11.99	14.00	16.01
$k \times 10^6$	4.91	5.66	5.90	5.98	6.06	6.11	6.17	6.25	6.06

Phthalic Acid (4).—(Acid = 0.01301 molar; alkali = 0.02779 molar.)

Phthalic Acid (5).—(Acid = 0.005198 molar; alkali = 0.01148 molar.)

<i>c.c. Alkali.</i>	$k_1 \times 10^6$.	$k_2 \times 10^6$.	<i>c.c. Alkali</i>	$k_1 \times 10^6$.	$k_2 \times 10^6$.
0 } 10 }	8.96	[5.06]	0 } 10 }	8.50	[4.93]
2 } 12 }	9.74	5.15	2 } 12 }	9.17	4.89
4 } 14 }	10.26	5.29	4 } 14 }	9.68	5.00
6 } 16 }	10.32	5.25	6 } 16 }	9.98	5.04
8 } 17 }	[10.20]	5.14	8 } 17 }	[9.67]	5.02

Phthalic Acid (6).—(Acid = 0.002599 molar; alkali = 0.005531 molar.)

<i>c.c. Alkali.</i>	$k_1 \times 10^6$.	$k_2 \times 10^6$.	<i>c.c. Alkali.</i>	$k_1 \times 10^6$.	$k_2 \times 10^6$.
0 } 10 }	7.67	[3.64]	6 } 16 }	8.06	3.99
2 } 12 }	7.75	4.03	8 } 17 }	[7.38]	3.87
4 } 14 }	8.11	4.08			

¹² Rabinowitch and Kargin, *Z. Electro-Chem.*, 1927, **33**, 11.

TABLE I.—*Continued.***Iso-Phthalic Acid (7).**—(Acid = 0.0007211 molar; alkali = 0.001595 molar.)

<i>c.c. alkali</i>	0 4	0 6	0 7	0 9	2 6	2 10	4 10	4 11	6 10	6 13
$k_1 \times 10^6$	1.95	1.96	1.97	1.98	1.95	2.00	2.06	2.06	2.14	2.17
$k_2 \times 10^5$	2.27	2.24	2.15	2.08	2.25	2.00	1.97	1.96	1.93	1.90

Hemi-Mellitic Acid (8).—(Acid = 0.03439 molar; alkali = 0.1105 molar.)

<i>c.c. alkali</i>	0 7 13	2 9 15	4 10 17	5 11 18
$k_1 \times 10^3$	1.39	1.55	1.59	1.59
$k_2 \times 10^5$	[7.61]	7.12	7.13	7.22
$k_3 \times 10^6$	[1.78]	1.85	1.83	1.79

Hemi-Mellitic Acid (9).—(Acid = 0.01712 molar; alkali = 0.05520 molar.)

<i>c.c. alkali</i>	0 7 13	2 9 15	4 10 17	5 11 17
$k_1 \times 10^3$	1.33	1.45	1.49	1.55
$k_2 \times 10^5$	6.80	6.42	6.34	6.17
$k_3 \times 10^6$	1.39	1.42	1.44	1.50

Hemi-Mellitic Acid (10).—(Acid = 0.008363 molar; alkali = 0.02704 molar.)

<i>c.c. alkali</i>	0 7 13	2 9 15	4 10 17	5 11 17
$k_1 \times 10^3$	1.22	1.34	1.39	1.40
$k_2 \times 10^5$	6.40	6.09	5.97	6.04
$k_3 \times 10^6$	1.22	1.28	1.29	1.29

Benzene Pentacarboxylic Acid (11).—(Acid = 0.01251 molar; alkali = 0.06846 molar.)

<i>c.c. Alkali.</i>	$k_1 \times 10^2$	$k_2 \times 10^3$	$k_3 \times 10^4$	$k_4 \times 10^6$	$k_5 \times 10^7$
0, 5, 9, 12, 16	1.55	1.84	1.17	7.37	5.36
1, 6, 10, 13, 17	1.58	1.87	1.18	7.48	5.23

Benzene Pentacarboxylic Acid (12).—(Acid = 0.009297 molar; alkali = 0.05073 molar.)

<i>c.c. Alkali.</i>	$k_1 \times 10^3$	$k_2 \times 10^3$	$k_3 \times 10^4$	$k_4 \times 10^6$	$k_5 \times 10^7$
3, 5, 9, 12, 16	1.53	1.70	1.07	6.98	4.55
2, 6, 10, 13, 17	1.53	1.66	1.08	7.01	4.88

Benzene Pentacarboxylic Acid (13).—(Acid = 0.004998 molar; alkali = 0.02742 molar.)

<i>c.c. Alkali.</i>	$k_1 \times 10^3$	$k_2 \times 10^3$	$k_3 \times 10^4$	$k_4 \times 10^6$	$k_5 \times 10^7$
1, 5, 8, 12, 16	1.18	1.58	.926	4.39	3.57
2, 6, 10, 13, 17	1.14	1.74	.815	4.89	3.97

TABLE I.—*Continued.***Mellitic Acid (14).**—(Acid = 0.01243 molar ; alkali = 0.08124 molar.)

<i>c.c. Alkali.</i>	$k_1 \times 10^3.$	$k_2 \times 10^3.$	$k_3 \times 10^4.$	$k_4 \times 10^5.$	$k_5 \times 10^6.$	$k_6 \times 10^7.$
1, 5, 7, 10, 13, 16	3.41	6.37	5.21	2.38	1.99	1.87
0, 4, 8, 11, 14, 17	3.35	6.13	5.28	2.40	2.02	1.67

Mellitic Acid (15).—(Acid = 0.008664 molar ; alkali = 0.05698 molar.)

<i>c.c. Alkali.</i>	$k_1 \times 10^3.$	$k_2 \times 10^3.$	$k_3 \times 10^4.$	$k_4 \times 10^5.$	$k_5 \times 10^6.$	$k_6 \times 10^7.$
0, 4, 7, 10, 13, 16	2.75	6.40	4.64	2.00	1.52	1.35
1, 5, 8, 11, 14, 17	2.93	6.25	4.60	2.01	1.63	1.11

Mellitic Acid (16).—(Acid = 0.004965 molar ; alkali = 0.03265 molar.)

<i>c.c. Alkali.</i>	$k_1 \times 10^3.$	$k_2 \times 10^3.$	$k_3 \times 10^4.$	$k_4 \times 10^5.$	$k_5 \times 10^6.$	$k_6 \times 10^7.$
2, 4, 7, 10, 13, 16	2.44	5.43	4.18	1.66	1.29	1.17
3, 5, 8, 11, 14, 17	2.64	5.87	3.80	1.62	1.31	1.09

A square bracket [] round a constant means that it is not a very reliable one as some factor used in its calculation, *e.g.* ($C\alpha - \omega$) has tended to approach zero, thus exaggerating experimental errors.

TABLE II.

Benzoic Acid (I.).

<i>Titre.</i>	<i>E.M.F.</i>	<i>Titre.</i>	<i>E.M.F.</i>	<i>Titre.</i>	<i>E.M.F.</i>	<i>Titre.</i>	<i>E.M.F.</i>	<i>Titre.</i>	<i>E.M.F.</i>
0.00	.1902	6.03	.1348	12.02	.1014	16.99	.0541	18.55	-.1165
2.00	.1649	8.03	.1237	14.01	.0885	18.03	.0173		
4.02	.1477	10.00	.1132	16.02	.0693	18.32	-.0161		

Benzoic Acid (II.).

0.00	.1873	6.03	.1341	12.00	.1014	17.01	.0527	18.42	-.043
1.99	.1639	8.01	.1231	14.03	.0879	18.01	.0159	18.45	-.057
4.00	.1474	10.02	.1123	16.00	.0688	18.34	-.024		

Benzoic Acid (III.).

0.00	.1779	6.02	.1324	11.99	.0997	16.99	.0501	18.44	-.011
2.00	.1597	8.02	.1215	14.00	.0864	18.05	.0166	18.51	-.070
4.02	.1448	10.00	.1109	16.01	.0663	18.24	.0068		

Phthalic Acid (IV.).

0.00	.2156	8.05	.1439	9.53	.1149	14.06	.0533	18.04	-.0135
2.00	.2018	8.53	.1354	10.05	.1045	16.04	.0304	18.33	-.028
4.00	.1871	9.05	.1251	12.06	.0748	17.02	.0150	18.64	-.060
6.02	.1693								

TABLE II.—Continued.

Phthalic Acid (V.).

<i>Titre.</i>	<i>E.M.F.</i>	<i>Titre.</i>	<i>E.M.F.</i>	<i>Titre.</i>	<i>E.M.F.</i>	<i>Titre.</i>	<i>E.M.F.</i>	<i>Titre.</i>	<i>E.M.F.</i>
0·00	·2015	8·00	·1393	10·03	·1022	16·02	·0285	18·34	—·027
2·00	·1906	8·53	·1307	12·00	·0734	17·03	·0129	18·54	—·045
4·00	·1783	9·02	·1217	14·00	·0518	18·01	—·0123	18·92	—·107
6·00	·1628	9·50	·1123						

Phthalic Acid (VI.).

0·00	·1896	8·03	·1302	10·01	·0964	15·99	·0245	18·30	—·027
1·98	·1797	8·50	·1225	11·99	·0691	17·00	·0088	18·83	—·063
3·98	·1684	9·03	·1134	14·03	·0473	18·00	—·015	18·97	—·076
6·03	·1531	9·52	·1048						

Iso-Phthalic Acid (VII.).

0·00	·1578	7·00	·1229	10·98	·0983	17·02	·0263	18·48	—·034
1·99	·1484	8·02	·1172	13·02	·0831	18·00	—·015	18·63	—·040
4·02	·1386	9·02	·1112	15·01	·0636	18·30	—·029	18·78	—·043
6·00	·1285	10·00	·1048						

Hemi-Mellitic Acid (VIII.).

0·00	·2346	6·00	·1622	10·01	·1104	13·03	·0640	18·02	—·0275
2·01	·2110	7·00	·1490	11·01	·0966	15·01	·0336	18·22	—·0366
4·00	·1877	8·99	·1235	11·99	·0814	17·00	·0010	18·51	—·0595
5·01	·1751								

Hemi-Mellitic Acid (IX.).

0·00	·2242	5·01	·1717	9·01	·1199	13·01	·0584	18·02	—·0349
2·01	·2047	6·03	·1586	11·01	·0922	15·01	·0264	18·22	—·0441
4·01	·1832	7·02	·1455	12·00	·0760	17·02	—·0069	18·53	—·0696

Hemi-Mellitic Acid (X.).

0·00	·2130	6·02	·1551	10·07	·1035	13·03	·0546	18·01	—·0383
2·00	·1970	7·04	·1423	11·02	·0898	15·06	·0222	18·34	—·0544
3·99	·1782	9·04	·1173	12·02	·0727	17·02	—·0107	18·62	—·0815
5·01	·1671								

Benzene Pentacarboxylic Acid (XI.).

0·00	·2449	5·03	·1990	10·01	·1164	14·54	·0304	18·38	—·102
1·01	·2377	6·02	·1854	10·54	·1061	15·07	·0201	18·50	—·128
2·00	·2299	7·00	·1698	11·02	·0968	16·00	·0007	18·60	—·141
2·99	·2210	7·50	·1613	12·03	·0773	17·02	—·0235		
3·53	·2156	8·04	·1520	13·06	·0582	18·02	—·0654		
4·02	·2103	9·02	·1346	14·03	·0399	18·26	—·085		

Benzene Pentacarboxylic Acid (XII.).

0·00	·2389	5·00	·1959	9·03	·1325	14·02	·0393	18·01	—·067
0·98	·2327	6·00	·1827	10·01	·1148	15·00	·0184	18·42	—·080
2·00	·2253	7·03	·1669	12·02	·0764	16·00	—·0017	18·74	—·112
2·98	·2169	8·01	·1503	13·00	·0582	17·03	—·0242	18·94	—·133
4·00	·2069								

Benzene Pentacarboxylic Acid (XIII.).

0·00	·2272	4·03	·1982	8·03	·1445	13·00	·0486	17·05	—·0327
1·02	·2211	5·01	·1881	9·02	·1267	14·04	·0284	18·04	—·063
2·03	·2146	6·02	·1762	10·01	·1062	15·03	·0091	18·31	—·076
3·01	·2078	7·00	·1616	12·00	·0656	16·03	—·0114	18·47	—·084

TABLE II.—*Continued.*

Mellitic Acid (XIV.).

<i>Titre.</i>	<i>E.M.F.</i>	<i>Titre.</i>	<i>E.M.F.</i>	<i>Titre.</i>	<i>E.M.F.</i>	<i>Titre.</i>	<i>E.M.F.</i>	<i>Titre.</i>	<i>E.M.F.</i>
0·00	·2529	5·01	·2097	9·01	·1356	12·50	·0556	15·99	—·0168
1·00	·2466	5·50	·2026	9·52	·1227	12·99	·0454	17·02	—·0442
1·98	·2396	6·03	·1950	10·01	·1107	14·02	·0242	17·51	—·0642
2·51	·2352	6·52	·1874	11·01	·0879	14·53	·0143	18·00	—·106
3·00	·2311	7·00	·1788	11·50	·0769	15·00	·0047	18·27	—·152
3·52	·2261	8·00	·1593	12·01	·0659	15·50	—·0059	18·44	—·167
4·00	·2211	8·49	·1479						

Mellitic Acid (XV.).

0·00	·2460	4·03	·2157	8·03	·1534	13·02	·0368	17·02	—·0570
1·02	·2398	5·04	·2040	9·02	·1295	14·00	·0166	17·52	—·081
2·04	·2329	6·02	·1901	10·02	·1045	16·00	—·0270	18·00	—·146
3·02	·2252	7·02	·1739	11·01	·0817				

Mellitic Acid (XVI.).

0·00	·2346	5·00	·1967	10·01	·1002	14·00	·0120	18·00	—·114
1·02	·2290	6·02	·1834	11·01	·0764	15·03	—·0096	18·16	—·129
2·00	·2228	7·00	·1684	12·00	·0541	16·02	—·0313	18·32	—·143
2·98	·2153	8·03	·1485	13·01	·0327	17·01	—·058	18·44	—·150
4·00	·2069	9·02	·1250						

Discussion of Results.

In comparing the several dissociation constants of an acid either with each other or with those of another acid, the thermodynamic constants should be used. The conclusions in the following discussion are not vitiated by the use of "imperfect" constants, since the effects could not be due to deviations from the laws of ideal electrolytes.

If we ignore the mutual influence of the carboxyl groups, simple statistical considerations give the relations :

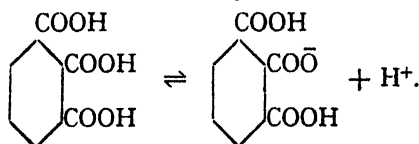
$$k_1 \text{ (mellitic)} : k_1 \text{ (benz. pentacarboxylic)} : k_1 \text{ (}h\text{-mellitic)} :$$

$$k_1 \text{ (phthalic)} : k_1 \text{ (}iso\text{-phthalic)} : k_1 \text{ (benzoic)} = 6 : 5 : 3 : 2 : 2 : 1$$

The ratios observed are much greater, and are of the order of

$$500 : 250 : 25 : 15 : 3 : 1.$$

These ratios indicate the tendency of one carboxyl group to promote the ionisation of another, an effect first observed by Walker¹⁸ for dibasic acids, and later confirmed in several cases. The ratios show, as might be expected, that the effect increases with the number of carboxyl groups, and the influence of the inter-group distance is evident in the different values of k_1 for phthalic and *iso*-phthalic acids. Further, it may be supposed that, owing to this promoting effect of carboxyl groups, those groups which contribute most hydron will be most central with respect to the other groups. *E.g.*, in the case of *hemi*-mellitic acid the following process will be the most important :



In mellitic acid each carboxyl group is equally central, and each of the six carboxyl groups will have a greater tendency to ionise than the most

¹⁸ Walker, *J. Chem. Soc.*, 1892, 61, 696.

active group in hemi-mellitic acid. The carboxyl groups in benzene pentacarboxylic acid are almost equally central, so that a similar consideration applies to this acid. These considerations probably account for the great increase in the value of k_1 observed on passing from hemi-mellitic to benzene pentacarboxylic and mellitic acids.

The tendency of an ionised carboxyl group —COO^- to hinder the ionisation of an unionised carboxyl group in virtue of its negative charge is also plainly shown. Thus, on purely statistical grounds we should expect :

$$k_1 (\text{benzoic}) : k_2 (\text{iso-phthalic}) : k_3 (\text{phthalic}) : k_4 (\text{h-mellitic}) : k_5 (\text{benz. pentacarboxylic}) : k_6 (\text{mellitic}) = 6 : 3 : 3 : 2 : 6/5 : 1.$$

The actual ratios found are much greater, and are of the order of

$$6000 : 2500 : 500 : 120 : 35 : 10.$$

The effect of distance is shown by the difference in the ratios for phthalic and *iso*-phthalic acids.

A more detailed discussion of the constants will be reserved till data for the remaining members of this series of acids has been obtained.

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NOTE ON THE POROSITY OF CHARCOAL.

BY ALEXANDER KING.

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A morphological theory of the porosity of active charcoal has been put forward by Burrage¹ on the assumption that the charcoal derived from cellulose is more easily oxidised than that from lignin, during the combustion of wood and in its subsequent activation. This has proved very valuable in explaining the greater activity of charcoals of vegetable origin, and in particular of wood charcoals, as compared with those from non-cellular sources, but it takes no account of the fact that charcoals formed from sugar, tartaric acid and other homogeneous materials are capable of activation in exactly the same manner, although not to such a high degree as wood charcoals. The pitting due to selective combustion of cellulose residues is of microscopic dimensions, and probably only produces an initial, roughly porous material in which the ultrapores, whose diameter has been shown² to be of about the same magnitude as mediumly large organic molecules, can be formed. The present note attempts to outline a simple and more general explanation of the porosity of all charcoals, activated or unactivated, which may be extended to the consideration of other porous systems.

There is still a certain amount of disagreement as to the structure of charcoal. Debye and Scherrer³ showed by means of X-ray examination that the so-called amorphous carbon was graphitic in structure, an

observation which has received ample confirmation. Nevertheless, Ruff and his co-workers⁴ criticise this point of view, and consider that amorphous carbon is a true modification, the adsorptive powers of charcoal being due to it and to it alone. The colour of charcoal, its thermal conductivity, its density which approximates to that of graphite if helium is used to measure it, the gradual transition to true graphite, the ease with which (as compared to graphite) it can be oxidised to graphitic acid—a material which possesses without doubt the graphite lattice⁵—and above all, examination by means of electron diffraction⁶ all lead to the conclusion that charcoal is essentially composed of unorientated micro-crystals of graphite.

When aliphatic organic materials such as sugar, cellulose, etc., are charred, therefore, they appear to give rise to more or less aromatic derivatives. A very drastic rearrangement must occur, with the momentary setting free of valencies. As large amounts of volatile tarry materials containing unsaturated derivatives are evolved during this stage of the charring, it is only natural that some of these should combine with the carbon to form surface compounds, the majority of which will probably be decomposed at a later stage in the combustion. The fact that charcoals can retain combined hydrogen at a high temperature does show, however, that some of these compounds are exceptionally stable.

When this satisfaction of free valencies of the carbon occurs, that part of the surface is prevented from growing further, or from coalescing with other graphite rings to form larger crystals, and thus remains exposed. Hence it seems unlikely that much hydrogen is contained in the carbon except at exposed surfaces. Analysis shows charcoals to contain quite large amounts of both oxygen and hydrogen, and it is probable that the initial char consists of small aggregates of graphitic crystals, having hydrogen, hydroxyl, or corresponding groups on practically all the crystal edges. This inhibition of crystal growth during formation and the random distribution of the crystals, accounts for the extreme porosity of charcoal as compared with any other substances where conditions favour the formation of a more or less uniform lattice.

The degree of porosity of a charcoal will depend on the extent of inhibition of crystal growth, and those charcoals which, like sugar charcoal are really cokes, having been solidified from the melt, evolving only small amounts of gas after they are solidified, *i.e.*, after the crystals have been formed, should be less porous and hence less active than wood charcoals where the transformation occurs in the solid state throughout.

The results quoted below refer to two charcoals. The first is a normal, unpurified sugar charcoal; the other was formed at the same temperature

ADSORPTION OF FATTY ACIDS (EQUIVS. $\times 10^{-5}$ PER GM.) ON CHARCOAL.

Adsorbent.	HCOOH.	CH ₃ COOH.	C ₂ H ₅ COOH.	C ₃ H ₇ COOH.	C ₄ H ₉ COOH.
Impure sugar charcoal . . .	27.6	29.3	34.7	24.7	19.2
Same after evacuation at 450° . .	29.9	37.8	51.1	38.1	30.0
Crude, molasses charcoal . . .	118	132	108	97.8	90.2
Same after evacuation at 450° .	122	171	176	188	178

and under exactly the same conditions, but the starting material was molasses. In the latter case, solidification took place at an early stage in the combustion, while large quantities of unsaturated fumes were still being evolved. As neither of these charcoals was formed from cellular materials, the mechanism proposed by Burrage cannot have come into operation.

The results show that the molasses charcoal was very much more active than the sugar charcoal, as we should expect from the conditions of its formation. Evacuation had a marked effect on both charcoals, but especially on that from molasses, which evolved much larger quantities of organic matter than did the sugar charcoal during evacuation. The expulsion of hydrocarbons must, therefore, still be recognised as an important factor in activation. It is worth noting also that the molasses charcoal was capable of being activated to as high a degree as the average sample of wood charcoal.

According to the point of view expressed above, all charcoals should exist in a state of extreme porosity even before activation, the differential combustion of different organic materials (and of the charcoals of different densities derived from them), both during carbonisation and activation, leading to enhanced activity in the case of wood charcoals. The process of activation is probably a complicated one, but consists essentially in the removal by oxidation of poisoning hydrocarbons with a consequent freeing of valencies and formation of active centres, together with a general extension of surface area and increase in size of the original pores owing to the removal of carbon by oxidation.

It is worth noting that silica gel, another substance of great porosity, is formed in a roughly similar manner to that just described for charcoal, namely, a rearrangement of molecules accompanied by gas evolution. Work will shortly be carried out in this laboratory on other systems of a similar nature to see whether a high degree of porosity can be produced.

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- ² King, *J. Chem. Soc.*, 1934, 1975.
- ³ Debye and Scherrer, *Z. physik. Chem.*, 1917, **18**, 291.
- ⁴ Ruff, Schmidt and Olbrich, *Z. anorgan. Chem.*, 1925, **148**, 313.
- ⁵ Hofmann, Frenzel and Csalan, *Annalen*, 1934, **510**, 1 (also appended bibliography).
- ⁶ Jenkins, *Phil. Mag.*, 1934, **17**, 457.

REVIEW OF BOOK.

Kolloidchemisches Taschenbuch. Edited by Dr. ALFRED KUHN.
(Leipzig: Akademische Verlagsgesellschaft M.B.H. Pp. viii + 369.
1935. Price RM. 19.)

The literal translation of the German title of this work is apt to mislead the English reader: it is too large for the pocket and neither in scope nor in matter resembles what the technical man understands by a pocket book. It is, in fact, a concise but very complete compendium of modern colloid

science, the work of sixteen collaborators who treat the subject in sixteen sections with the headings: Concepts and systematics of colloid science (Ostwald); Preparation of colloidal systems (Kuhn); Protection and sensitisation (Kuhn); Kinetics of disperse systems (Fürth); Dialysis, filtration and ultrafiltration (Rheinboldt); Optics of disperse systems (Zocher, Wiegner, v. Susich); Shape of colloid particles (Söllner); Phenomena at boundaries (Haller, v. Buzágh); Electric phenomena (Auerbach); Colloids as electrolytes (Valkó); Coagulation (Pallmann); Dissolution and peptisation (v. Buzágh); Solvation (Haller, Kuhn, Küntzel); Mechanical properties of gels (Söllner); Chemical reactions in jellies (Erbring); Determination of particle sizes (Gessner).

It will be seen how completely the ground is covered; details of the arrangement are open to criticism. Thus viscosity appears as a sub-heading in the section on solvation, although it is a fundamental property which can be measured, whereas solvation is a matter of definition, inference or conjecture. On the whole the general editor has been very successful in carrying out one of his more difficult duties: that of preventing individual authors from magnifying their office excessively, but he has not been able to avoid completely a feature common to most collective works, an occasional lack of proportion. Thus an allowance of twenty-two pages for the Tyndall phenomenon seems perhaps excessive compared with the same number of pages devoted to dialysis, filtration and ultrafiltration, or a mere dozen pages allotted to the electrical properties of disperse systems. A good deal of space is also taken up by the classification and nomenclature of the—not very happily named—"diffuse" systems, nomenclature which is hardly required and gives the enemy cause to blaspheme. The same remark applies to the terminology of gels in Section XIII (Solvation): it is difficult to see what is gained by calling a jelly produced by swelling "oedogenous"; it may perhaps be pleaded in extenuation that the term is at least all Greek, in contrast to the terrible "solvatocratic."

These, however, are trifles which, moreover, have been characteristic of much of the recent German literature on colloids. Apart from the individual excesses just mentioned, the editor has managed to get a uniform terminology and even a consistent style adopted by his team of contributors. Incidentally, one curious statement appears in his own chapter on sol formation, where the decomposition of nickel carbonyl in benzene, which leads to the formation of a nickel organosol, is described as hydrolysis, although no water is present.

The proof reading has been done with extraordinary care, and the book is well printed and adequately illustrated. It is certainly calculated to fulfil the purpose stated in the preface: that of providing chemists, physicists, biologists and medical men with a means of surveying quickly and thoroughly the various fields of colloid science.

E. H.

ERRATUM.

In the review of *Solid Geometry*, by L. Lines, in the June number the name of the publishers was wrongly given. They are Macmillan & Co.

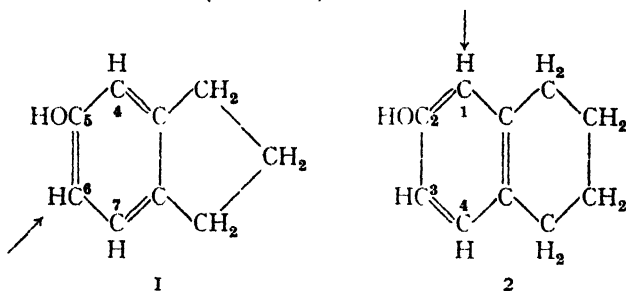
A WAVE-MECHANICAL TREATMENT OF THE MILLS-NIXON EFFECT.

BY L. E. SUTTON AND L. PAULING.

Received 8th April, 1935.

Contribution No. 444 from the Gates Chemical Laboratory, California Institute of Technology, Pasadena, California.

In 1930, W. H. Mills and I. G. Nixon¹ showed that by attaching saturated carbon rings of different sizes to two *ortho* valencies of a benzene molecule it is possible to make the benzene ring react as though it had either one or other of the two Kekulé structures. Thus, they found that 5-hydroxyhydrindene undergoes substitution by bromine or by diazo residues in the 6 position, and so behaves as though the benzene ring in this compound had that Kekulé structure with the single bond common to the two rings (formula 1), whereas *ar*-tetrahydro- β -naphthol undergoes these substitutions in the 1 position, and so behaves as though it had the other structure (formula 2).



These facts they explained by pointing out that since the angle between two single bonds is less than that between a single bond and a double bond, when the bonds come from a four-covalent van't Hoff-le Bel atom (the angles being $109^{\circ} 28'$ and $125^{\circ} 16'$, respectively) the angles between successive pairs of external valencies of a single benzene structure should alternate, as shown in Fig. 1, angle α being less than angle β . They then stated that, while in ordinary benzene there could be a tautomerism between the two Kekulé structures with equal concentrations of both present, if two adjacent valencies are pulled together (as they would be if a five-membered ring were attached to them) one structure—the one with the single bond between the valencies in question—is made much more stable than the other, and predominates.

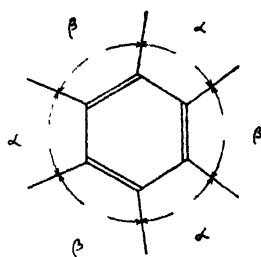


FIG. 1.

¹ Mills and Nixon, *J. Chem. Soc.*, 1930, 2510.

In this way Mills and Nixon explained the behaviour of 5-hydroxyhydrindene. The reason for the behaviour of *ar*-tetrahydro- β -naphthol could not be expressed so simply, but they advanced arguments from a comparison of the strains in the two structures to show that when a six-membered ring is attached the structure with the double bond common to the two rings is the more stable, although according to their calculations the difference is small and vanishes if the angle between the valencies of a methylene group is 112.8° .

The conception of the benzene molecule which has been developed from the ideas of wave mechanics calls for some modification of the above interpretation of the facts. Two approximate methods of treatment have been applied to the problem of the structure of benzene, the method of molecular orbitals and the method of valency-bond wave functions²; the results of these are essentially in agreement.³ In our discussion of the present problem we shall make use of the second method, inasmuch as the first one does not offer an approach to it. It appears very definitely that benzene is a single molecular species and from the second method we can say that it is a hybrid of the two Kekulé structures and various excited structures, and that the angles between the pairs of external valencies are all 60° . In the wave function for the whole molecule, the wave functions corresponding to the two Kekulé structures occur with equal coefficients, because these structures, regarded as separate entities, have equal energies. If, however, two *ortho* valencies are displaced from a mutual inclination of 60° , the two Kekulé structures no longer correspond to equal energies; if the angle is increased the structure with the double bond between the *ortho* valencies in question, hereinafter called structure I, will have the lower energy and its coefficient will therefore increase, while that of the other structure, hereinafter called structure II, will decrease. The reverse will occur if the angle is decreased. Owing to the great energy corresponding to resonance between the two structures, these changes of coefficient will, however, be relatively small.

In order to treat the problem quantitatively we shall ignore the excited structures (whose contribution to the resonance energy is small), and shall set up and solve the quadratic secular equation for the wave functions of the two Kekulé structures. In the simple treatment of benzene,² the matrix elements $H_{I,I}$ and $H_{II,II}$ are both equal to $Q - W + \frac{3}{2}\alpha$, and the elements $H_{I,II}$ and $H_{II,I}$ are equal to $\frac{1}{2}(Q - W) + \frac{3}{2}\alpha$, Q being the Coulomb energy, W the total energy, and α the exchange integral, which has the value 34,000 cal./gm. mole. This Q includes the strain energy caused by altering the angles of the two *ortho* valencies from ϕ_I or ϕ_{II} to 60° . In the present problem its value is different in the different matrix elements, and therefore it is necessary to express the strain energy explicitly in each. The strain energy in $H_{I,I}$ is that which there would be if the molecule had structure (I) only, *i.e.*, $\frac{1}{2}k(\phi - \phi_I)^2$ where k is a force constant and ϕ_I is the angle between the unstrained valencies in structure (I). Similarly in $H_{II,II}$ it is $\frac{1}{2}k(\phi - \phi_{II})^2$. In the resonance integrals $H_{I,II}$ and $H_{II,I}$ it may reasonably be assumed that it is approximately the mean of those in the two structures, *i.e.*,

$$\frac{1}{4}K[(\phi - \phi_I)^2 + (\phi - \phi_{II})^2].$$

² Slater, *Physic. Rev.*, 1931, **38**, 1109; *ibid.*, **37**, 489; Hückel, *Z. Physik.*, 1931, **70**, 204; Pauling, *J. Chem. Physics*, 1933, **1**, 280; Pauling and Wheland, *ibid.*, 1933, **1**, 362.

³ Wheland, *J. Chem. Physics*, 1934, **2**, 476.

The secular equation is therefore :

$$\begin{vmatrix} Q' - W + \frac{1}{2}k(\phi - \phi_I)^2 + \frac{2}{3}\alpha & \frac{1}{2}\{Q' + \frac{1}{2}k[(\phi - \phi_I)^2 + (\phi - \phi_{II})^2] - W\} + \frac{2}{3}\alpha \\ \frac{1}{2}\{Q' + \frac{1}{2}k[(\phi - \phi_I)^2 + (\phi - \phi_{II})^2] - W\} + \frac{2}{3}\alpha & Q' - W + \frac{1}{2}k(\phi - \phi_{II})^2 + \frac{2}{3}\alpha \end{vmatrix} = 0.$$

For numerical roots to be obtained, values must be ascribed to ϕ_I , ϕ_{II} , and k .

The natural values of the angles γ (or δ') and δ (or γ') shown in Figs. 2 and 3, are $109^\circ 28'$ and $125^\circ 16'$, respectively. These values cannot be achieved simultaneously because the benzene angle is 120° .

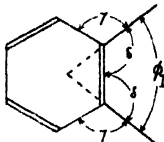


FIG. 2.

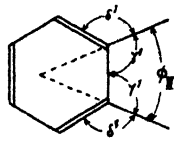


FIG. 3.

If we assume that the strain is equally divided between γ and δ and between γ' and δ' , we are led to the values $\phi_I = 75.5^\circ$ and $\phi_{II} = 44.5^\circ$. k is a bending force constant; since the bending of each bond is one half of the total, say $\frac{\phi - \phi_I}{2}$, the total bending energy is $a \frac{(\phi - \phi_I)^2}{4}$, where

a is the energy necessary to bend one bond through 1° , and therefore $k = a/2$. According to Stuart⁴ a is 16 cal./gm. mole. for the C—H bond in hydrogen cyanide, and hence $k = 8$ cal./gm. mole. We shall use this value for our C—C bonds in default of a better one.

The secular equation has been solved for $Q' - W$, with ϕ assuming values between 45° and 75° , and the ratios of the coefficients κ_I and κ_{II} of the wave functions for structures I and II in the wave function of the actual molecule, $\psi = \kappa_I\psi_I + \kappa_{II}\psi_{II}$, have been evaluated. The resonance energy, E , is the difference between W and Q (Q includes the strain energy), and since it can easily be shown that in this case

$$W \cong Q + \frac{1}{8}\alpha(1 - \frac{2}{3}\delta^2), \quad \text{where} \quad \delta = \frac{\kappa_{II}}{\kappa_I} - 1,$$

E can be calculated, and also ΔE , the change of resonance energy relative to that in normal benzene, wherein $\phi = 60^\circ$ and κ_{II}/κ_I is unity. From

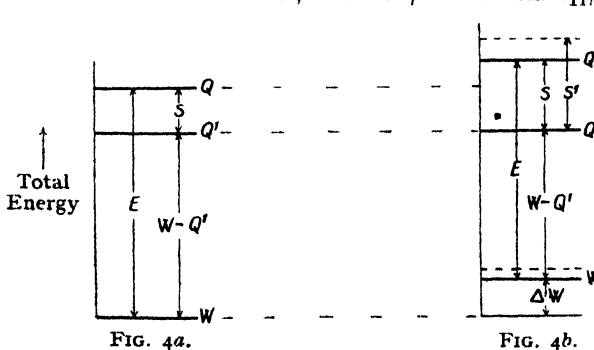


FIG. 4a.

FIG. 4b.

the strain energy S can be calculated for any value of ϕ , and can be compared with that, S' , which there would have been if κ_{II}/κ_I had remained equal to unity; this latter quantity is the mean of the strain energies in I and II for any particular value of ϕ , which is equal to the sum of the strain in normal benzene (961 cal./gm. mole.) and the quantity $\frac{1}{2}k(\phi - 60^\circ)^2$. The stability of the molecule as a whole, relative

⁴ Stuart, *Molekülstruktur*, Springer, Berlin, 1934, p. 86.

to normal benzene, is given by the differences in total energy, ΔW . The energy relations involved are illustrated in Figs. 4a and 4b, 4a showing the situation in normal benzene and 4b that in a strained benzene. Fig. 4a is explained by the foregoing and so is most of Fig. 4b; the upper broken line, in the latter, shows the value which Q would have if κ_{II}/κ_I remained equal to unity, and the lower broken line shows what the total energy would have been if also the resonance energy had been the same as in normal benzene. The values of these quantities for a series of values of ϕ are collected together in Table I.; the energies are expressed in cal./gm. mole.

TABLE I.

ϕ .	W .	ΔW .	κ_{II}/κ_I .	E .	ΔE .	S .	S' .	$\Delta S'$.	$S' - S$.
45°	$Q' - 79,784$	855	1.063	- 81,552	48	1,768	1,861	900	- 93
50°	$Q' - 80,259$	380	1.041	- 81,579	21	1,320	1,361	400	- 41
55°	$Q' - 80,543$	96	1.020	- 81,595	5	1,052	1,061	100	- 9
60°	$Q' - 80,639$	0	1.000	- 81,600	0	961	961	0	0
65°	$Q' - 80,543$	96	0.980	- 81,595	5	1,052	1,061	100	- 9
70°	$Q' - 80,259$	380	0.960	- 81,579	21	1,320	1,361	400	41
75°	$Q' - 79,784$	855	0.941	- 81,552	48	1,768	1,861	900	- 93

It will be observed that the resonance energy is decreased numerically by the change in κ_{II}/κ_I , but that the strain energy is decreased about twice as much by this same cause, so that the nett result is that the destabilisation of the molecule by the bending of the bonds is slightly less than it would have been if κ_{II}/κ_I had remained equal to unity or if there had been no resonance at all.

The changes in κ_{II}/κ_I are relatively small, and it remains to discuss whether or not they could account for the experimental facts. If a five-membered ring is attached to two *ortho* valencies of benzene the sum of the bond angles has to decrease from $568^\circ 24'$ to 540° , and if the simplifying assumption be made that the reduction of each bond angle is equal, this means that ϕ is reduced by about 12° , i.e., to about 48° , and therefore that κ_{II}/κ_I is approximately 1.05. This 5 per cent. change in the ratio of the coefficients of the two Kekulé structures is small. It may well be large enough, however, to cause one of the two substitution reactions to be favoured over the other to the extent shown by experiment. Thus we need only recall the important effects of substituents in the benzene ring in influencing the rates of further substitution in order to obtain support for the view that a small influence exerted on the benzene ring can produce important changes in rates of reaction. It is not unreasonable to expect that the effect consists primarily in a change in the heat of activation. If we represent the activation energy for the reaction of substitution in position 4 of the hydrindene derivatives by A_I and that for position 6 by A_{II} (these corresponding to positions 1 and 3 of the tetrahydronaphthalene derivatives), we may tentatively assume, in order to make a quantitative calculation, that the ratio A_I/A_{II} is given by the equation

$$\frac{A_I}{A_{II}} = \left(\frac{\kappa_{II}}{\kappa_I} \right)^2,$$

the occurrence of the second power being characteristic of wave-mechanical calculations. In the absence of pronounced steric effects, it

is probable that the ratio of the rates r_I and r_{II} of the reactions is given by the expression

$$\frac{r_{II}}{r_I} = \frac{e^{-A_{II}/RT}}{e^{-A_I/RT}}, \quad \text{whence} \quad \frac{r_{II}}{r_I} = e^{\frac{A_{II}}{RT} \left[\left(\frac{\kappa_{II}}{\kappa_I} \right)^2 - 1 \right]}.$$

Since a 5 per cent. increase in κ_{II}/κ_I produces a 10 per cent. increase in the square, it follows that the ratio anticipated for the rates of reaction would be $e^{0.1 A_{II}/RT}$, and if A_{II} lies between 10,000 and 20,000 cal./gm. mole., as is probable, the rate ratio is between 5 and 27, approximately. Thus, since the ratio of the quantities of product is that of the rates of reaction, the product of reaction II would form between 83 per cent. and 96.5 per cent. of the total yield.

The prediction of the effect of attaching a six-membered reduced ring is less simple, owing to the more complex steric relations. Our procedure here is different from that of Mills and Nixon,¹ for they assumed that the molecule had *either* structure I *or* structure II, whereas we consider that initially it has the symmetrical resonating structure and then calculate how much it is distorted when a ring is attached. The reduced ring cannot have a stable configuration in which it is coplanar with the benzene ring: the carbon atoms 6 and 7 may either be both on one side of this plane or one on either side. Assuming the carbon-carbon distances⁵ to be 1.39 Å in the benzene ring and 1.54 Å elsewhere, it is found on calculation that the *ortho* valency angle is decreased for the first configuration and increased for the second. The resultant total strain energy is less for the second than for the first configuration by about 300-500 cal./gm. mole. Moreover, it is known empirically that cyclohexane derivatives⁶ and 1.4-dioxane⁷ exist predominantly in the "Z" or chair form, presumably because of steric repulsion of the hydrogen atoms of the methylene groups. Therefore it is very probable that tetrahydronaphthalene and its derivatives also exist predominantly in the second configuration, which is approximately a "Z" configuration. For this configuration the angle ϕ is increased by 10° to 70°, κ_{II}/κ_I becomes 0.96, and the ratio of the rate of reaction I to that of reaction II will, on the previous hypothesis, be $e^{0.08 A_I/RT}$, which for values of A_I between 10,000 and 20,000 cal./gm. mole. is 3.8 to 14.5, so that the product from reaction I should form from 79 per cent. to 93.5 per cent. of the total yield.

The exact experimental facts as adduced by Mills and Nixon are the following. The bromination of 5-hydroxyhydrindene goes smoothly to give the 6-bromo derivative, with very little, if any, by-product, and 90 per cent. of the coupling of it with diazotised *p*-chloroaniline takes place in the 6 position; the coupling with diazotised *p*-toluidine also occurs mainly in the 6 position but gives a small quantity of by-product which although not identified completely is isomeric with the main product.¹ Bromination of 5-acetoamido-hydrindene yields the 6-bromo derivative only, judging by the description of the reaction given by Borsche and Bodenstein.⁸ The only product isolated in the bromination

⁵ Pauling and Brockway, *J. Chem. Physics*, 1934, 2.

⁶ Dickinson and Bilicke, *J. Am. Chem. Soc.*, 1928, 50, 764; Hassel, *Trans. Faraday Soc.*, 1934, 30, 874.

⁷ Schwingel and Greene, *J. Am. Chem. Soc.*, 1934, 56, 653; Sutton and Brockway, *ibid.*, 1935, 57, 473.

⁸ Borsche and Bodenstein, *Ber.*, 1926, 59, 1910.

of *ar*-tetrahydro- β -naphthol is the 1-bromo derivative the structure of which was decided by elimination rather than by direct determination.⁹ Coupling with diazotised sulphanilic acid occurs only in the 1 position; no definite mono-nitro derivative can be prepared because of the ease with which poly-nitration occurs; sulphonation is anomalous, occurring readily and completely in the 3 position.⁹ Two mono-bromo derivatives are obtained directly from 2-acetamido-tetrahydronaphthalene, one in 82 per cent. yield and the other in 12 per cent.;¹⁰ one must have the bromine atom attached to position 1 and the other must have it on position 4, but there is no direct chemical evidence to show which is which. It should be observed, however, that since the base derived from the main product is more volatile in steam than the other, it must certainly have the bromine atom on the 1 position, *i.e.*, *ortho* to the amino group, because *o*-chloro and *o*-bromoanilines are more volatile than the *m*- or *p*-compounds.¹¹ Thus it may be said that the brominations and diazo couplings go to the extent of 90 per cent. or more in the 4 position of the hydrindene derivatives, and to a similar extent in the 1 position of the tetrahydronaphthalene derivatives. There is, therefore, good agreement between the experimental facts and the theoretical predictions which have just been made. This shows that the wave-mechanical concept of the structure of the benzene molecule is capable of accounting for the facts interpreted by Mills and Nixon in terms of stabilisation of the individual Kekulé structures. It may be pointed out also that our treatment is based on the old contention that for some purposes, and within limitations, the substitution reactions of benzene derivatives can be discussed by considering the properties of the double bonds of the Kekulé structures.

One further question which merits discussion is that of the effect which forcibly altering the angle between two *ortho* valencies would have upon the angles between the other four. On the classical ideas it would obviously be expected that if the angle between one pair were fixed at ϕ then the angles between the alternate pairs would also be ϕ . Using wave-mechanical ideas the method of answering the question is the following. The expression for the total energy W ,

$$W = \frac{\int (\kappa_I \psi_I + \kappa_{II} \psi_{II}) H (\kappa_I \psi_I + \kappa_{II} \psi_{II}) d\tau}{\int (\kappa_I \psi_I + \kappa_{II} \psi_{II})^2 d\tau},$$

consists, when evaluated, of the Coulomb terms and exchange terms. The sum of the former terms has already been subdivided into two parts, the strain energy of a pair of external valencies, and the remainder of the energy, but this latter can be further subdivided, inasmuch as it also contains strain energy terms for the other two pairs of external valencies, the sum of which is

$$\frac{2\left\{\kappa_I^2 \frac{k}{2}(\phi' - \phi_I)^2 + \frac{\kappa_I \kappa_{II}}{2} \frac{k}{4}[(\phi' - \phi_I)^2 + (\phi - \phi_{II})^2] + \kappa_{II}^2 \frac{k}{2}(\phi' - \phi_{II})^2\right\}}{\kappa_I^2 + \frac{1}{2}\kappa_I \kappa_{II} + \kappa_{II}^2},$$

ϕ' being the angle between either of the two alternate pairs. In order to get the minimum energy, when κ_{II}/κ_I has been fixed by the forcible

⁹ Schroeter, *Annalen*, 1922, 426, 83.

¹⁰ Smith, *J. Chem. Soc.*, 1904, 85, 730.

¹¹ Sidgwick and Rubie, *J. Chem. Soc.*, 1921, 119, 1013; Fittig and Mager, *Ber.*, 1874, 7, 1179; *ibid.*, 1875, 8, 364; Nemurowski, *Ber.*, 1891, 24, ref. 271; Holleman, *Rec. Trav. chim. Pays Bas*, 1906, 25, 186. We are indebted to Professor H. J. Lucas for suggesting this line of argument.

bending of one pair, this sum must be minimised with respect to ϕ' , and from the differential relation which we thereby obtain the equilibrium value of ϕ' for any value of κ_{II}/κ_I can be calculated:—

$$\phi' = \frac{1}{2}(\phi_I + \phi_{II}) + \frac{1 - (\kappa_{II}/\kappa_I)^2}{2 + (\kappa_{II}/\kappa_I) + 2(\kappa_{II}/\kappa_I)^2}(\phi_I - \phi_{II}).$$

For $\phi_I = 75.5^\circ$, $\phi_{II} = 44.5^\circ$, and $\kappa_{II}/\kappa_I = 1.063$, ϕ' is found to be $59^\circ 15'$, and for $\kappa_{II}/\kappa_I = 0.941$, ϕ' is $60^\circ 45'$. It is seen that the bending of two valencies affects the disposition of the other four to only a very small extent. There are at present no published data by which this conclusion can be tested, and since the introduction of substituents in order to obtain such data from, say, measurements of electric dipole moment or electron-diffraction photographs would usually cause complications, as most substituents set up resonance of types other than that considered above, the interpretation of the results might be by no means straightforward.*

Summary.

The Mills-Nixon effect has been examined by a very simple wave-mechanical treatment. This has led to the conclusion that the effect of saturated side rings upon the ratio of the coefficients of the wave-functions of the two Kekulé structures is relatively small, being not more than about 6 per cent., and that the benzene ring retains the greater part of its stabilising resonance energy. Nevertheless, making the reasonable assumption that the ratio of the activation energies, for reaction as either one of the two Kekulé structures, depends upon the square of the ratio of coefficients, it is possible to account for the experimental facts. The effect which bending two valencies has upon the angles between the other valencies projecting from the benzene ring is found to be very small.

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* It may be pointed out, however, that although certain complications might be expected to arise in the previous considerations relating to the phenolic derivatives, there was no apparent indication of this happening.

THE COVALENCY ANGLES OF OXYGEN AND SULPHUR IN SOME ORGANIC COMPOUNDS.

BY L. E. SUTTON AND G. C. HAMPSON.

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The methods of determining the covalency angles of oxygen and sulphur in certain aromatic compounds from measurements of electric dipole moment, as used by Bergmann and his co-workers,^{1, 2} Smyth and Walls,³ and the present authors,^{4, 5} have recently been criticised

¹ Bergmann, Engel and Sandor, *Z. physikal. Chem.*, B, 1930, 10, 397.

² Bergmann and Tschudnowsky, *ibid.*, B, 1932, 17, 107.

³ Smyth and Walls, *J. Amer. Chem. Soc.*, 1932, 54, 3230.

⁴ Hampson and Sutton, *Proc. Roy. Soc., A*, 1932, 140, 562.

⁵ Hampson, Farmer, and Sutton, *ibid.*, A, 1933, 143, 147.

by Bennett.^{6, 7} In view of this and of the fact that further experimental data are now available, it seems desirable to review the subject carefully, and to see what are the most reasonable conclusions which may at present be drawn.

The methods having already been fully described elsewhere,^{4, 5} it is only necessary to say here that values of the oxygen covalency angle have been calculated in two types of ether, diphenyl ether and anisole, and that of the sulphur angle in diphenyl sulphide. The methods for both types of compound depend for their significance not only upon the accuracy with which the moments may be determined, but also upon the validity of the assumption that the moments arising from interaction between the oxygen atom and the substituent groups are negligible, *i.e.*, that the moment produced by substituting the group X by the group Y is the moment of $p\text{-X} \cdot \text{C}_6\text{H}_4 \cdot \text{Y}$. In compounds of the anisole type there is the further assumption that the moment of the phenoxy-group, μ_{PhO} , is the same in anisole as in diphenyl ether, and if, further, the angle in dimethyl ether be calculated, a third assumption, that the moment of the methoxy-group, $\mu_{\text{CH}_3\text{O}}$, is equal in anisole and dimethyl ether, has to be made. After examining the available data, the present authors concluded that the first assumption was sufficiently near to the truth for the results to be of value, provided that the substituent group was methyl or a halogen, but Bennett argues that for these also the interaction moments are so great that the results are quite worthless. He does not criticise the second assumption but, instead, he too makes it in the course of demonstrating how far wrong the first one is.

We agree with Bennett that there is now evidence of appreciable interaction not only between strong groups of the two opposite orienting types, the *ortho-para* and the *meta* orienting, but also between the halogens, which are *ortho-para* directing, and the very strong groups of the same type, such as $-\text{OCH}_3$, $-\text{NH}_2$, and $-\text{N}(\text{CH}_3)_2$. This is shown in the anisoles by the systematic variation of the angle ϕ , to which Bennett has called attention, in the anilines by a similar variation,^{8, 4, 6} and in the dimethyl-anilines by the moments of 3.29 and 3.37 which have been found for the *p*-chloro- and *p*-bromo- derivatives⁹ and which are greater than the maximum values 3.14 and 3.10, calculated on the extreme assumption that the moment of dimethyl-aniline is parallel to the N-Ph direction. There appears to be no evidence of it in the phenols,¹⁰ for in these the values of ϕ , with $-\text{CH}_3$, $-\text{Cl}$, and $-\text{Br}$ as substituents, are all concordant. It may be remarked that although it is possible, as Bennett argues, that the interaction moment would be the same for several groups, and so remain undetected if the variation of ϕ be taken as the criterion of its existence, it is very unlikely, on general grounds, that this would actually happen.

Granting the existence of these interactions, we must proceed to consider qualitatively the effect which they will have upon the values calculated for the valency angles of oxygen and sulphur. For this purpose, we need to know the directions and relative magnitudes of the interaction moments for different groups, and we agree with Bennett

⁶ Bennett and Glasstone, *Proc. Roy. Soc., A*, 1934, **145**, 71.

⁷ Bennett, *Trans. Faraday Soc.*, 1934, **30**, 853.

⁸ Bergmann and Tschudnowsky, *Z. physikal. Chem., B*, 1932, **17**, 100.

⁹ R. J. B. Marsden, private communication.

¹⁰ Donle and Gehrckens, *Z. physikal. Chem., B*, 1932, **18**, 306.

that for the groups $-\text{NO}_2$, $-\text{I}$, $-\text{Br}$, $-\text{Cl}$, and $-\text{F}$, they are all in the positive sense relative to the $-\text{OCH}_3$ group,* *i.e.*, are parallel to the moments of the substituents, and decrease in the order given. The effect in question has already been discussed to some extent by the present authors, who derived an expression which showed whether the error in the value from the mono-substituted ether was greater or less than that in the value from the di-substituted one, and also whether or not it was of the same sign: in particular, it was shown that if

$$1 + \mu_S/(\mu_O \cdot \cos \rho)$$

is negative, *i.e.*, if $\mu_S > \mu_O$ and if $\rho > 90^\circ$, they will be of opposite signs, so that the true value of the angle must lie between the two observed values. The reason for this is immediately obvious from the vector diagrams below:

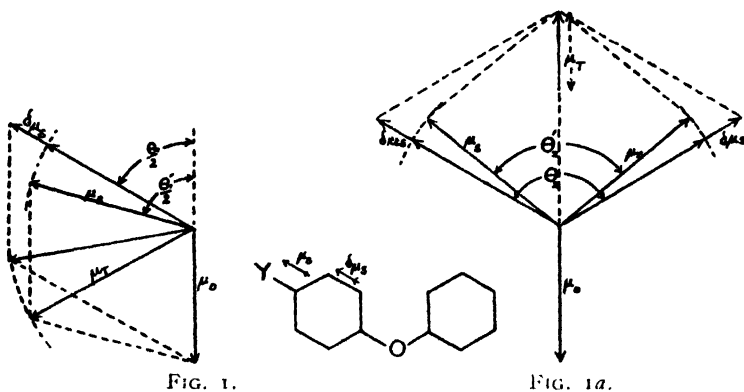


FIG. 1.

FIG. 1a.

Fig. 1 represents the case where $\rho > 90^\circ$, as for the mono-substituted compound; $\theta_1/2$ is the incorrect angle, calculated on the assumption that no interaction moment arises, θ_1 is the correct one, obtained when the extra moment $\delta_1\mu_S$ is introduced to give the complete vector diagram. When $\delta_1\mu_S$ is in the negative sense relative to the benzene ring, as shown, $\theta_1' > \theta_1$, *i.e.*, the uncorrected angle is too large. In the di-substituted compound, however, the error is in the opposite direction if the interaction is of the same type, as shown in Fig. 1a, and $\theta_2' < \theta_2$. It follows that this should be true for the angles derived both from the nitro- and bromo-ethers. The errors in those from the tolyl-ethers will be of the same sign, however, which will be negative or positive according as $\delta\mu_S$ is positive or negative relative to the C—O— link, as shown in Figs. 2 and 2a.

The angle derived from the mono-nitro-ether is indeed obviously too large, being greater than 180° , and it follows that the value of $122\text{--}123^\circ$ calculated from the di-nitro-ether must be too small. Of the three moments entering into the latter calculation, those of diphenyl ether,

* This convention is derived from the one already used for the sign of the moment of a substituent group (Sutton (16)). If the group specified is imagined to be on the right-hand side of the benzene ring, when the latter is viewed from a direction at right angles to its plane, then a movement of electrons towards this group, caused by interaction with another one, being a movement of *negative* charge in a *positive* direction, will correspond to a *negative* interaction moment, and a movement away will correspond to a *positive* one.

nitrobenzene, and *p*, *p'*-di-nitro-diphenyl ether, 1.16-1.17, 3.93, and 2.60-2.62 respectively, only the first is likely to be appreciably in error from neglected atom polarisation, and it may readily be seen that the effect of this error (which always makes the observed moments too large) would also be to make the calculated value of θ_2 too small; hence 122° may be taken as the minimum possible value for θ unless some error, non-existent in analogous compounds, affects this result.

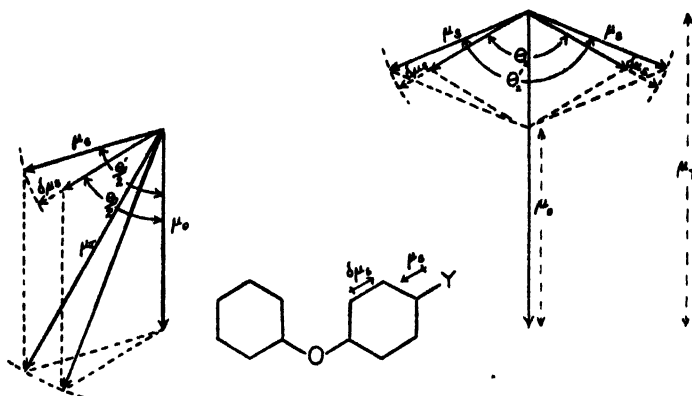


FIG. 2 and 2a.

We would expect that in the bromo-ethers there would be the same qualitative effects, but that the errors would be smaller than those in the nitro ethers, and the value of $141-144^\circ$ given by the monobromo ether is obviously in harmony with this prediction. In deriving an angle from the di-bromo-ether, we have to solve the difficulty of deciding whether its moment and that of the parent ether are parallel or anti-parallel, the corresponding calculated values of θ_2 being 155° and 112.5° respectively. Previously the former alternative was chosen⁵ because it gave a value nearer to that from the mono-bromo ether, but since, as we now see, there is reason to expect θ_2 to be less than, and not greater than, θ_1 we now consider that the second alternative is correct, and that the discrepancy which exists between this lower value and that from the di-nitro-ether is due to error from neglected atom polarisation. Of the three relevant moments, those of diphenyl ether, bromobenzene, and *p*, *p'*-dibromodiphenyl ether, 1.16-1.17, 1.52, and 0.52 respectively, the first and the third are most liable to this error, and it may readily be seen that its presence in either or both of these moments would cause the calculated value of θ to be too small, on the second of the alternative assumptions.*

Although the value of the atom polarisation is known for but few compounds with any accuracy, it now appears very unlikely that it exceeds 7 c.c. in most organic molecules; in many quite complex ones it is 2.5 c.c., and in particular the best value for di-ethyl ether is 3.4 c.c.^{11, 12} The values for the angles have therefore been recalculated allowing for an atom polarisation of 5 c.c. in the dibromo ether (where the error is most serious) and the results are included in Table I.

* It is true that on the first alternative, atom polarisation error in the third moment would make the calculated angle too large, but any in the first moment would tend to counteract this.

¹¹ Sugden, *Trans. Faraday Soc.*, 1934, **30**, 734.

¹² Jenkins, *idem.*, p. 739.

TABLE I.*

No.	μ_0 .	μ_S .	μ_T .	θ
1.	Diphenyl ether.	Bromobenzene.	Monobromo-di-phenyl ether.	142° 40'
2.	Diphenyl ether.	Bromobenzene.	Dibromo-diphenyl ether.	111°
2a.	Diphenyl ether.	Bromobenzene.	P_A allowance.	123° 30'
3.	Diphenyl ether.	Toluene.	Monotolylphenyl ether.	153° 50'
4.	Diphenyl ether.	Toluene	Di- <i>p</i> -tolyl ether.	142°
5.	Diphenyl ether	Nitrobenzene.	Mononitro-di-phenyl ether.	> 180°
6.	Diphenyl ether.	Nitrobenzene.	Dinitro diphenyl ether.	122° 30'
7.	Dibromo-diphenyl ether	<i>p</i> -Bromotoluene.	Di- <i>p</i> -tolyl ether.	119° 20'
7a.	P_A allowance.	<i>p</i> -Bromotoluene	Di- <i>p</i> -tolyl ether.	128° 30'
8.	Di- <i>p</i> -tolyl ether	<i>p</i> -Bromotoluene.	<i>p</i> -Bromo- <i>p</i> -tolyl ether.	139°

* Values of moments taken, in benzene as solvent ¹³ —

Diphenyl ether.	1.16	Monotolyl-phenyl ether	1.31
Monobromo-diphenyl ether.	1.59	Ditolyl ether.	1.42
Dibromo-diphenyl ether	0.56	Bromobenzene	1.52
Allowing $P_A = 5$ c.c.	0.28	Toluene.	0.40
<i>p</i> -Bromophenyl- <i>p</i> -tolyl ether.	1.98	<i>p</i> -Bromotoluene	1.96
Mononitro-diphenyl ether	4.29	Nitrobenzene	3.93
Dinitro-diphenyl ether.	2.62		

It follows from the foregoing argument that solutions 1, 3, 4, 5, and 8 are too high, whilst 2, 2a, 6, 7, and 7a are too low.

In order to determine narrower and more precise limits within which the angle should lie, we must attempt to make allowance for the effect of interaction error. If we assume that the interaction moments are the same in the mono- and the di-substituted ethers (*i.e.*, $\delta_1\mu_S = \delta_2\mu_S$) the formulæ given previously ⁵ may be applied.* The necessary data and the results are given in Table II. Table II. also contains the results

TABLE II

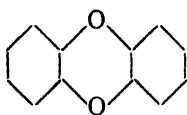
Parent Ether and Substituent Groups	$\delta_1\mu_S = \delta_2\mu_S$		$\delta_1\mu_S = 2\delta_2\mu_S$	
	θ .	$\delta_1\mu_S$.	θ .	$\delta_1\mu_S$
Diphenyl ether : nitro.	132°	0.70	128°	0.76
Diphenyl ether : bromo.	122°	0.26	118°	0.32
P_A	129.5°	0.17	127°	0.19
Diphenyl ether : methyl.	121°	0.14	138°	0.07
Di- <i>p</i> -tolyl ether : bromo.	126°	0.21	123°	0.23
P_A	132°	0.12	130.5°	0.14

¹³ "A Table of Dipole Moments," *Trans. Faraday Soc.*, 1934, **30**, Appendix.

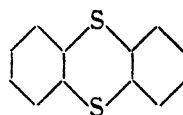
* It is also tacitly assumed that the interaction in one benzene ring does not affect the other; this is probably not exactly true, but probably is so to a first approximation.

obtained when the other extreme assumption, namely that $\delta_1\mu_S = 2\delta_2\mu_S$ is used.† Since the value of $\delta_1\mu_S/\delta_2\mu_S$ almost certainly lies between 1 and 2,⁵ the results given in Table II. represent new limits for θ . The values obtained from the methyl substituted compounds and diphenyl ether are very susceptible to small differences in the values taken for the moments, and so are not very reliable. Bearing this in mind, and also the possible effect of observational errors, and the uncertainties of the argument, it appears that the best value for the oxygen angle in diphenyl ether is $128^\circ \pm 4^\circ$.

Complete qualitative confirmation of such a large value is provided by the fact that diphenylene dioxide



(unlike thianthrene)



has no measurable moment, which means that the molecule must be planar and hence that the oxygen valency angles must be at least 120° .¹⁴

The only remaining source of error to be discussed is the solvent effect. If either the Müller or the Jenkins empirical rules, for the effect of a solvent upon the value of the moment of a solute observed in it,¹⁵ apply to the above ethers in the solvent used (benzene) the solvent action will not affect the values calculated for the angles, for each moment will be expressible as $k\mu_{\text{vapour}}$, where k depends only upon the solvent, and the coefficient will cancel in the expressions for the angles. It has been pointed out to us by Mr. F. C. Frank that it is not even necessary that the solvent effect should be proportionately the same upon all the separate moments, for there to be no effect of the solvent upon the calculated angles: it is only necessary that in any one solvent the original moment, μ_O , and the substitution moments, μ_S , should be definite in magnitude and direction. Thus, for example, provided that the effective, observable moment of the C—O—C group is the same in diphenyl ether as it is in the derivatives, and that that of C—Br is the same in bromobenzene as in the bromo-ethers, in one solvent, the resultant moments will depend only upon these values and upon the oxygen angle, and a true value of the latter will be derivable from them. Since the groups in the *para* positions in a benzene ring are about 6 Å.U. apart, it is reasonably probable that this condition is satisfied, to a first approximation. In order to test the matter experimentally, the moments of a series of ethers have been measured in *n*-hexane and, as may be seen from the results in Table III., they give essentially the same values for the angles as do the moments in benzene.

The data for the thio-ethers may be analysed similarly to those for the ethers. If the moments of diphenyl sulphide and *p*, *p'*-dichlorodiphenyl sulphide are assumed to be anti-parallel, the angle from these compounds, 96° , is smaller than that from the parent substance and the *p*-monochloro-derivative 118 – 121° . This would be expected since the interaction moment would, by analogy with the ethers, be in the direction of the substitution moment. Part of the difference is almost certainly

† The equations representing this state of affairs lead to a cubic equation which can be solved for θ and $\delta_1\mu_S$.

¹⁴ Bennett, Earp, and Glasstone, *J. Chem. Soc.*, 1934, 1179.

¹⁵ Müller, *Physikal. Z.*, 1933, 34, 689; Jenkins, *Nature*, 1934, 133, 106.

due to atom polarisation error in the small moment of 0.58 found for the di-chloro-derivative: making an allowance of 5 c.c. for this, the lower value is increased to 109° , which is a probable lower limit. The value from the di-tolyl sulphide is intermediate between the upper and lower limits, being $112-118.5^\circ$, as is reasonable. Thus these results also fall into a coherent scheme and do so more readily than do those for the ethers because there is only one moment which is small enough to need much correction. If, now, the allowance for interaction be made as before, we find that if $\delta_1\mu_S/\delta_2\mu_S = 1$, $\theta = 114^\circ$ and $\delta\mu_S = 0.10$, while if $\delta_1\mu_S/\delta_2\mu_S = 2$, $\theta = 113^\circ$ and $\delta_1\mu_S = 0.16$. The sulphur valency angle in diphenyl sulphide therefore appears to be $113 \pm 3^\circ$, allowing for experimental error.

From the above values of the angles, the moments of the Ph—O and Ph—S groups (including the moments induced in the phenyl groups), in

TABLE III.—*n*-HEXANE AS SOLVENT.

No.	μ_O .	μ_S .	μ_T .	θ
1.	Diphenyl ether	Bromobenzene.	Monobromo-diphenyl ether.	152°
2.	Diphenyl ether.	Bromobenzene.	Dibromo-diphenyl ether.	110°
2a.	Diphenyl ether	Bromobenzene	P_A allowance.	120°

Allowing for Interaction.

Parent Ether and Substituent Groups	$\delta_1\mu_S = \delta_2\mu_S$		$\delta_1\mu_S = 2\delta_2\mu_S$	
	θ	$\delta_1\mu_S$	θ .	$\delta_1\mu_S$.
Diphenyl ether · bromo. P_A	124°	0.35	119°	0.40
	130°	0.29	126°	0.34

Values of moments in *n*-hexane as solvent (see experimental section):—Diphenyl ether, 1.18; *p*-monobromo-diphenyl ether, 1.75; *p-p'*-dibromo-diphenyl ether, 0.65; P_A , 0.43.

diphenyl ether and diphenyl sulphide, are 1.33 ± 0.09 and 1.36 ± 0.05 respectively.

If μ_{Ph-S} and the sulphur angle be assumed to have the same mean values in thianthrene, the moment calculated for this compound* is 1.27; altering the angle in thianthrene to 110° gives 1.47, and to 116° gives 0.99. Since the differences of angle are so small and it is quite possible that the angle may be smaller in thianthrene than in diphenyl sulphide this discrepancy is insignificant.

From the empirical rule suggested by one of the present authors,^{16, 17} the moment of the Ph—O group should be numerically less than that of the $(CH_3)_3C—O$ group. The former is 1.33 ± 0.09 ; the latter has not been determined directly, but a rough value may be calculated from the

* $\mu_{Thianthrene} = 4\mu_{Ph-S} \sqrt{\cos^2 \theta/2 - 1/4}$.

¹⁶ Sutton, *Proc. Roy. Soc., A*, 1931, **133**, 668.

¹⁷ *Ibid.*, *Trans. Farad. Soc.*, 1934, **30**, 795.

CH_3O group moment. This moment, taking that of dimethyl ether as 1.32 and the oxygen angle as $111^\circ \pm 3^\circ$ (see later), is 1.18 ± 0.04 , and in order to derive the required moment, allowance must be made for the moments induced in the $\text{C}-\text{C}$ bonds: this may be done crudely by assuming that $\mu(\text{CH}_3)_2\text{C}-\text{O}/\mu\text{CH}_3\text{O} = \mu(\text{CH}_3)_2\text{C}-\text{Cl}/\mu\text{CH}_2\text{Cl}$, whence $\mu(\text{CH}_3)_2\text{C}-\text{O} = 1.35 \pm 0.05$. This case does not fit the rule very strikingly therefore, but does so well enough, considering the approximations involved.

For the anisoles, unfortunately, it is not possible to evaluate the angle so satisfactorily, because it is not possible to calculate both upper and lower limits for it. As a consequence, the values further deduced for the aliphatic ethers must also be erroneous. There are three errors, other than those of observation, which affect the angle calculated in

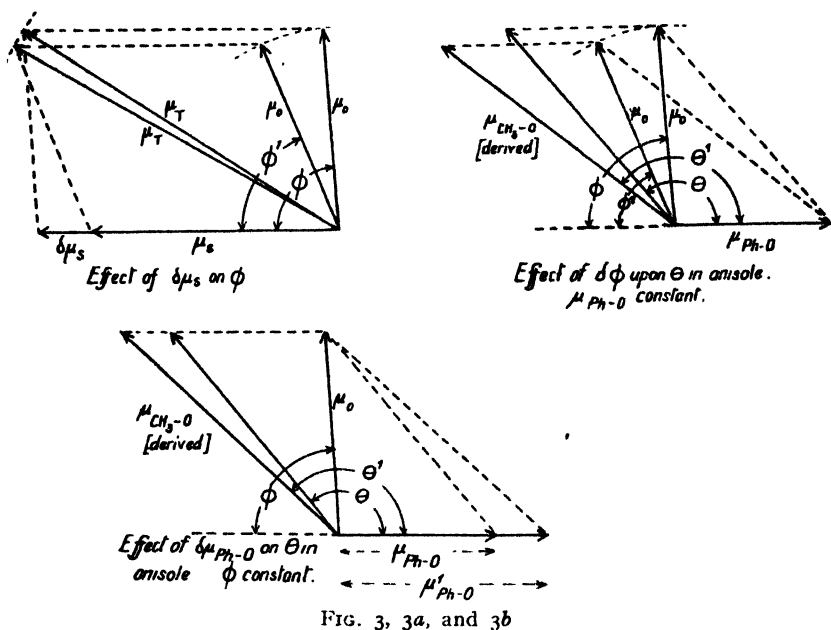


FIG. 3, 3a, and 3b

anisole (i) atom polarisation error, (ii) interaction error, (iii) error in the moment taken for the $\text{Ph}-\text{O}$ group. Regarding their effects, it suffices to say here that the effect of the first would be to make the angle ϕ too large, and therefore θ too small, but it would be relatively unimportant. The second error, if the interaction moment is negative, will make ϕ too small and θ too large, and this will be augmented by the effect of the third error if, as is very probable, $\mu_{\text{Ph-O}}$ is larger in diphenyl ether than in anisole,* see Figs. 3, 3a and 3b. These errors can be important. The angle calculated for dimethyl ether will be affected similarly and, in addition, since the moment of the CH_3O group is likely to be greater in anisole than in dimethyl ether, because of the effect of resonance (see later), the effect of erroneously assuming it to be the same will be to increase the calculated angle still further. While fairly satisfactory allowances might be made for the first two errors, this cannot be done

* Because in the former the oxygen has to resonate with two benzene nuclei, in the latter with only one.

for the third, so at present there is no satisfactory method of finding the angle in anisole, nor, by implication, in phenol.

The only other experimental method which has been applied so far to determine the angle in diphenyl ether is the matching of observed and calculated collision areas, as developed by Hare and Mack.¹⁸ It gave the angle as 107° , but the value of this result is uncertain.*

Four methods have been applied to determine the angle in aliphatic ethers. The first one was the collision area method, which gave about 110° in dimethyl ether. The next two involved the analysis of electric dipole moment data: the procedure of Allen and Hibbert¹⁹ and of Bennett^{6, 7} was to assume that $\mu_{\text{C-O}}$ is equal in ethylene oxide and in dimethyl ether, to calculate it from the former compound, the configuration of which was taken as known, and then to find what angle in the latter compound would give the observed moment; the value was 115° . The procedure of Smyth and Walls³ and of Hampson, Farmer, and Sutton⁵ was to use data for the anisoles, as already described; it gave a value of 147° . The fourth method was to use the diffraction of electrons by the vapour; Brú²⁰ obtained a value of 100° , and Sutton and Brockway²¹ one of $111^\circ \pm 4^\circ$. The weight of the first value is uncertain, as is also that of the second for, as regards the latter, the ring strain may affect $\mu_{\text{C-O}}$ in ethylene oxide, the moment may not be col-linear with the bond (if unshared oxygen electrons contribute much to it) and the change of the inductive effect of one C—O bond upon another, as the angle is changed, may be appreciable.

The third value is certainly wrong, but the last one is believed to be trustworthy, and shows that in this compound the angle actually is near to the tetrahedral angle. The same angle is found in chlorine monoxide²¹ (cf. ²²), but such a value appears to be larger than the "natural" angle of di-covalent oxygen, for that in water is 105° .²³ Since it was also found²¹ that the angle in methylene chloride was $111^\circ \pm 2^\circ$, and that the Cl—Cl distances in this compound and in chlorine monoxide are approximately equal, being respectively 2.92 ± 0.02 Å and 2.82 ± 0.03 Å, it appears that the bending force constant of an oxygen valency is approximately equal to that of a carbon valency and not, as had been tentatively suggested,^{5, 24} much smaller.

If, then, we assume as Bennett did, that the angles in all types of ethers should be 109.5° , the results for diphenyl ether, from dipole measurements, are decidedly anomalous. Consequently, either the dipole method breaks down for the ethers or the above assumption must be wrong. We favour the latter alternative. While there would be no reasons for expecting a marked difference, on classical principles, when the effects of quantum resonance are taken into account it appears not merely possible but even probable that the angle will vary in different

¹⁸ Hare and Mack, *J. Amer. Chem. Soc.*, 1932, **54**, 4272.

* A reduction in the calculated shadow areas by 2.4 per cent. would lead to a larger angle, ca. 115 – 130° being found.

¹⁹ Allen and Hibbert, *Ber.*, 1932, **65**, 1366; *J. Amer. Chem. Soc.*, 1934, **56**, 1398.

²⁰ Brú, *Anales soc. españ. fís. quim.*, 1932, **30**, 486.

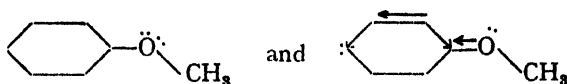
²¹ Sutton and Brockway, *J. Amer. Chem. Soc.*, 1935, **57**, 473. These effects may be responsible for the apparently anomalous variation of the moments of the di-, tri-, tetra-, and penta-methylene oxides.¹⁹

²² Bailey and Cassie, *Proc. Roy. Soc., A*, 1933, **142**, 129. By an oversight no reference was made to this paper in ²¹.

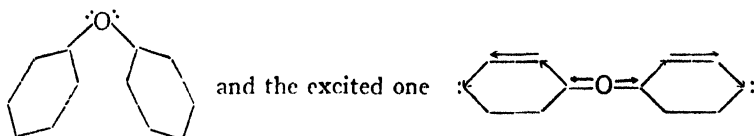
²³ Mecke, *Z. Physik*, 1933, **81**, 313; Mecke and Baumann, *ibid.*, 445.

²⁴ Sidgwick, *Trans. Farad. Soc.*, 1934, **30**, 859.

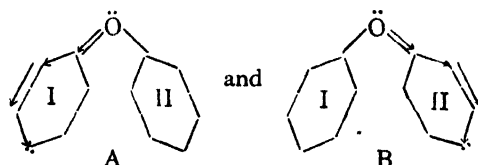
types of ether. In anisole there would be resonance between the two types of structure



which would cause the angle to approach 125° ^{16, 25, 17}. In diphenyl ether there might be resonance between the simple structure



which would cause the angle to approach 180° : more probably, as Professor L. Pauling has pointed out in conversation, the important excited resonant structures would be



It is obvious that this could cause a widening of the angle to 125° , and on closer examination it may be seen that it would cause an even greater widening. In structure A, ring I would be held in the plane containing the two valencies to oxygen, while in structure B ring II will be held in this plane. Since both of these must coexist equally, it follows that both rings in the hybrid molecule will be held co-planar with a rigidity which depends upon the resonance energy, *i.e.*, upon the importance of the excited structures relative to the simple one. Now, resonance of the simple form with either one of the equivalent excited forms alone should cause the angle to approach 125° , but since the actual resonance should tend to keep both rings coplanar, the angle may be further increased to a value such that the two nearest hydrogen atoms are at their distance of closest approach, if the resonance energy is sufficient, *i.e.*, to a value of from 123.5° to 145° , according to the thickness of the envelope by which the repulsions of electrons are represented.^{5*} The observed angle falls within this range. It is obvious that this type of resonance would also account for the planar configuration of diphenylene dioxide, wherein the oxygen angle has to be at least 120° . Moreover, the probability of its occurrence in di-hydrophenazine would lead us to expect that this compound, or its derivatives, would be planar too.

If the latter of the two hypotheses is correct, then it would be expected that in general in compounds of the type Ph_2X , whenever there is resonance between the bridging atom or group X and the two benzene rings, the angle will be increased, and that if the distance C—X is approximately the same as that of C—O, and if the resonance energy is

⁵ Pauling and Sherman, *J. Chem. Physics*, 1933, 1, 606.

* These are calculated taking the following values for the distances: C—O 1.47 Å.U., C—C 1.39 Å.U., C—H 1.14 Å.U., H—H 0.74 Å.U., envelope 0—0.5 Å.U.

approximately equal to that in diphenyl ether, the angle $\text{Ph}-\text{X}-\text{Ph}$ will be about 130° . In benzophenone the angle is, indeed, reported as 131° - 134° by Bergmann, Engel, and Meyer;³⁸ we have redetermined the moments of *p*-chlorobenzophenone and *p*, *p'*-di-chlorobenzophenone as 2.71 and 1.70 which, taking the moment of benzophenone as 2.95, give $\theta = 131^\circ$ and 133° , thus confirming Bergmann's result. The very close agreement between these values indicates that there is no appreciable interaction error. Similarly, for 1, 1-diphenyl-ethylene, they find the angle to be 127° , and using their data for the *cis* and *trans* *p*-chloro- and *p*-bromo- 1, 1-diphenyl-vinyl bromides, we have calculated θ in these compounds to be 144° and 154° (these are probably too large, because of interaction error).⁴ The small angles of $115 \pm 5^\circ$ in diphenyl methane and $112 \pm 10^\circ$ in diphenyl sulphoxide,⁵ on the other hand, agree with the fact that no such resonance would be expected in these compounds. The angle of $113 \pm 3^\circ$ found in diphenyl sulphide may have a similar significance, but the angle between a single and a double bond to sulphur is not necessarily equal to that between the same bonds to an element in the first short period *; it may be less: moreover, the angle range for the rings to be co-planar is 111 - 131° , owing to the greater radius of the sulphur atom. There is, therefore, sufficient evidence in support of the hypothesis to warrant its being given careful consideration.

It may be pointed out that this explanation of the enlargement of the angle leads to the possibility that the angle in, say, diphenyl ether, might vary according to the nature of the substituent groups. Thus in *p*-*p'*-dinitro-diphenyl ether the two nitro groups would augment the resonance of the type postulated, as is shown by the large interaction moments, and by thus causing the rings to be held more firmly in a plane, might further increase the angle. In view of the concordance of the angle values given by the different substituents, it appears likely, however, that in diphenyl ether this effect is not marked, possibly because the resonance in the unsubstituted ether is already so strong that the angle is near its maximum value.

Experimental.

Diphenyl ether and the mono- and dibromo-derivatives were prepared and purified as described in a previous paper.⁵

p-Tolyl-*p*-bromophenyl ether was prepared by heating 20 gms. of potassium *p*-cresylate with 30 gms. *p*-dibromobenzene and 7 gms. of *p*-cresol and a little copper bronze, in a dry flask with an air condenser, to 200°C . The reaction may be vigorous, and is soon over (one hour).

The product was steam distilled to remove unchanged dibromobenzene, the residue was extracted with ether, and the extract was dried with calcium chloride. After distilling off the ether the product was fractionally distilled under reduced pressure. The fraction boiling below 210° at 24 mm. pressure was collected, leaving behind a high-boiling fraction, probably $\text{CH}_3 \cdot \text{C}_6\text{H}_4 \cdot \text{O} \cdot \text{C}_6\text{H}_4 \cdot \text{O} \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_3$ (some of this high-boiling fraction was crystallised from alcohol and shown to be free from bromine). The distillate was again fractionated under reduced pressure to remove this impurity and then crystallised four times from methyl alcohol and centrifuged. It gave white nacreous plates m.p. 68.2 - 68.7°C . (corr.).

Found C = 59.42 per cent., H = 4.02 per cent., Br = 30.29 per cent.
Calculated C = 59.32 per cent., H = 4.21 per cent., Br = 30.38 per cent.

³⁸ Bergmann, Engel, and Meyer, *Ber.*, 1932, 65, 446.

* The angle between the two single bonds in hydrogen sulphide has just been determined to be $92^\circ 20'$, from infra-red spectrum analysis, by Cross (*Physic. Rev.*, 1935, 47, 7).

p-Mono and *p*-*p'*-Di-chlorobenzophenone were kindly supplied by Mr. T. W. J. Taylor. The m.p.s. were 74° and 146° C. respectively.

n-Hexane. B.D.H. "Pure for Spectroscopy" quality was refluxed and distilled from phosphorus pentoxide.

Electric Dipole Moment Measurements.

The measurement of the electric dipole moments was carried out as previously described, and the symbols have their usual significance.^{10, 6} Tables IV. and V.*

TABLE IV.

f_z	d_z^{25}	ϵ	P_z
<i>Diphenyl ether in n-Hexane at 25.0° C.</i>			
0.038078	0.6846	1.9570	80.96
0.031464	0.6813	1.9456	81.28
0.020949	0.6759	1.9264	81.11
0.014067	0.6724	1.9144	81.62
0.0	0.6652	1.8891	(81.7)
<i>p-Monobromo-diphenyl ether in n-hexane at 25.0° C.</i>			
0.028888	0.6947	1.9811	120.4
0.020461	0.6862	1.9552	121.7
0.014280	0.6798	1.9360	123.6
0.009484	0.6749	1.9201	123.5
0.0	0.6652	1.8891	(124.6)
<i>p-p'-Dibromo-diphenyl ether in n-hexane at 25.0° C.</i>			
0.038447	0.7258	1.9444	78.5
0.024519	0.7039	1.9242	78.6
0.019408	0.6959	1.9171	78.8
0.012564	0.6852	1.9067	77.7
0.0	0.6652	1.8891	(78.8)
<i>Bromobenzene in n-hexane at 25.0° C.</i>			
0.038202	0.6900	1.9827	86.3
0.024738	0.6812	1.9495	86.8
0.021604	0.6793	1.9414	86.6
0.018071	0.6769	1.9333	87.1
0.0	0.6652	1.8891	(87.5)

TABLE V.

f_z	d_z^{25}	ϵ	n_D^{25}	P_z	kP_z
<i>p-Bromophenyl-p-tolyl ether in Benzene at 25.0° C.</i>					
0.017288	0.8920	—	2.26845	—	67.1
0.012680	0.8873	—	2.26537	—	67.1
0.011168	0.8858	2.3416	2.26449	148.0	67.1
0.009932	0.8845	2.3340	2.26398	148.1	67.6
0.006552	0.8811	2.3131	2.26123	148.1	66.6
0.005496	0.8799	2.3070	—	149.5	—
0.0	0.8742	2.2727	2.25712	(148.5)	(67.1)
<i>p-Monochlorobenzophenone in Benzene at 25.0° C.</i>					
0.019987	0.8877	2.4913	2.27307	208.3	63.6
0.015299	0.8845	2.4410	2.26949	210.4	63.6
0.011931	0.8822	2.4043	2.26701	211.8	63.7
0.007393	0.8791	2.3545	2.26355	213.3	63.6
0.0	0.8741	2.2727	2.25797	(216.2)	(63.6)
<i>p-p'-Dichlorobenzophenone in Benzene at 25.0° C.</i>					
0.018577	0.8914	2.3619	2.27434	126.3	68.6
0.014509	0.8876	2.3428	—	127.0	—
0.011461	0.8846	2.3281	2.26797	127.2	68.9
0.006662	0.8801	2.3050	—	127.8	—
0.0	0.8738	2.2727	2.25797	(128.6)	(68.8)

Substance.	T^{P_1} .	E^{P_2} .	$A \quad O^{P_2}$.	μ .
Diphenyl ether.	81.7 c.c.	52.7* c.c.	29.0 c.c.	1.18D
<i>p</i> -Monobromo-diphenyl ether.	124.6	61.0*	63.6	1.75
<i>p-p'</i> -Dibromo-diphenyl ether.	78.8	70.0*	8.8	0.65
Bromobenzene.	87.5	34.5	53.0	1.60
<i>p</i> -Bromophenyl- <i>p</i> -tolyl ether.	148.5	67.1	81.4	1.98
<i>p</i> -Monochlorobenzophenone.	216.2	63.6	152.6	2.71
<i>p-p'</i> -Dichlorobenzophenone.	128.6	68.8	59.8	1.70

* Values taken from solutions in benzene ⁵

Summary.

The methods of determining the valency angles of oxygen and sulphur in the ethers and thio-ethers by electric dipole moment determinations have been carefully reconsidered, and it has been concluded that they can give fairly accurate results in diphenyl ether and diphenyl sulphide if properly applied. The angles in these compounds are now found to be $128^\circ \pm 4^\circ$ and $113^\circ \pm 3^\circ$ respectively. The large value in the former agrees with the fact that diphenylene dioxide is non-polar. Since the oxygen valency angle in dimethyl ether and chlorine monoxide is about 112° , this large angle in the aromatic compounds is evidently abnormal. An explanation of its occurrence is proposed, based upon the probable resonance of the ordinary structure with others in which the oxygen atom forms a double bond with one nucleus. It is shown that there is evidence for similar enlargements of angle in analogous compounds, as would be required by this explanation.

The moments of diphenyl ether, its *p*-mono- and *p-p'*-di-bromo-derivatives, and bromobenzene have been determined in *n*-hexane at 25.0° C., and have been found to be 1.18, 1.75, 0.65, and 1.60 respectively. Those of *p*-bromophenyl-*p*-tolyl ether, *p*-mono- and *p-p'*-di-chlorobenzophenone in benzene at 25.0° C. have been found to be 1.98, 2.71, and 1.70 respectively.

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THE NO⁺ RADICAL.

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The first suggestion of the existence of the NO⁺ radical was made by Hantzsch in 1909.¹ He observed that the molecular weight of nitrosyl sulphate (nitrosylsulphuric acid) determined cryoscopically in sulphuric acid solution was anomalously low. Values ranging from 70.8 to 72.5 were obtained, compared with the value of 127 calculated from the empirical formula, HNSO₅. He concluded, therefore, that in sulphuric acid this substance behaves as an electrolyte and suggested that dissociation into NO⁺ and HSO₄⁻ ions took place.

Twenty-one years later Hantzsch and Berger² compared the properties of nitrosyl perchlorate and nitrosyl sulphate and concluded that both these substances existed as salt-like compounds, [NO⁺][X⁻], where X is the perchlorate or acid sulphate group.

Proof of the validity of their conclusion was obtained by conductivity measurements on nitrosyl perchlorate in nitromethane, but they were unable to determine corresponding data for nitrosyl sulphate because of its very limited solubility in nitromethane. This work will later be discussed more fully.

The recent investigation by the authors of the Raman spectra of nitrosyl sulphate and nitrosyl perchlorate gave results which can be interpreted only on the assumption that these substances have an ionic structure. This work will be reviewed briefly in the next section.

Before proceeding to a discussion of experimental data it will be necessary to consider the theoretical possibility of the existence of such a radical as NO⁺. The most important criterion is the ease with which a neutral molecule can lose an electron and become positively charged. To bring about this ionisation a certain ionisation potential is required, and it follows that the lower the ionisation potential the greater the probability of the existence of that particular ion. For nitric oxide the ionisation potential is 9.5 volts.³ The ionisation potential of N₂ → N₂⁺ is very much higher. Values of about 17 volts were obtained by Foote and Mohler,⁴ Brandt,⁵ and Hogness and Lunn.⁶ More recent values, owing to improved technique, are lower by about 1 volt. Vaughan⁷ finds the value of 15.8 volts in agreement with Found,⁸ Boucher,⁹ and Turner and Samson.¹⁰ Although the most recent value is 15.65 volts,¹¹

¹ *Z. physik. Chem.*, 1909, **65**, 57.

² *Z. anorg. Chem.*, 1930, **190**, 321.

³ Tate and Smith, *Physic. Rev.*, 1932, **39**, 270—9.5 volts; Mackay, *Physic. Rev.*, 1924, **24**, 319—9.4 volts; Hughes and Dixon, *Physic. Rev.*, 1917, **10**, 495—9.38 volts; Hogness and Lunn, *Physic. Rev.*, 1927, **30**, 26—9 volts.

⁴ Foote and Mohler, *J. Opt. Soc. Amer.*, 1920, **4**, 49.

⁵ Brandt, *Z. Physik*, 1921, **8**, 32.

⁶ Hogness and Lunn, *Physic. Rev.*, 1925, **26**, 786.

⁷ Vaughan, *ibid.*, 1931, **38**, 1687.

⁸ Found, *ibid.*, 1920, **16**, 41.

⁹ Boucher, *ibid.*, 1922, **19**, 189.

¹⁰ Turner and Samson, *ibid.*, 1929, **34**, 747.

¹¹ Tate, Smyth and Vaughan, *ibid.*, 1933, **43**, 1054.

and about 10 per cent. lower than the previous value, it is very considerably higher than the value for $\text{NO} \rightarrow \text{NO}^+$. The ionisation potential for $\text{O}_2 \rightarrow \text{O}_2^+$ is also very much higher than for $\text{NO} \rightarrow \text{NO}^+$. Mulliken and Stevens¹² conclude that the ionisation potential of O_2 is 12.2 volts, somewhat lower than the values obtained by previous experimenters.¹³ Without enumerating further examples for diatomic molecules, which are, in general, above 10 volts, it is clear that for the particular molecule under consideration the ionisation potential is decidedly low. This may arise from the fact that NO is an odd-electron molecule having 15 extranuclear electrons. When this molecule becomes ionised it is isoelectronic with two diatomic molecules possessing great stability, CO and N_2 . Since isoelectronic structures exhibit many similar properties it is possible that the NO^+ radical is a relatively stable one. From the experimental evidence discussed in the next two sections its existence seems to be unquestionable.

Raman Spectra Data and the Frequency of NO^+ .

The authors have recently completed investigations of the Raman spectra of nitrosyl sulphate¹⁴ and nitrosyl perchlorate.¹⁵ Spectra were obtained for the solid substances and for solutions of nitrosyl sulphate in various concentrations of sulphuric acid and solutions of nitrosyl perchlorate in various concentrations of perchloric acid. In all the spectra for the solids a Raman displacement of 2330 cm^{-1} appeared very prominently. This displacement also occurred in the solutions of higher concentration of the appropriate acid and persisted in more dilute acid solutions so long as the substances were incompletely hydrolysed.

For nitrosyl perchlorate four other displacements in addition to the 2330 cm^{-1} displacement were observed. These could be assigned definitely to the ClO_4^- ion since they had been observed previously in perchlorates. This, therefore, indicates the presence of the ClO_4^- ion in nitrosyl perchlorate, and it follows that the remaining frequency, absent from the spectra of perchloric acid and perchlorates, must arise from the positively charged part of the molecule, the NO^+ group.

The spectrum of nitrosyl sulphate was much more complicated, containing frequencies some of which are found in pure sulphuric acid and others in pure nitric acid. One well-defined frequency of 1045 cm^{-1} plays an important rôle in deciding the structure of the molecule of nitrosyl sulphate. This frequency is not obtained in 100 per cent. H_2SO_4 but appears as soon as the acid is diluted. It is also a very intense frequency in the spectra of acid sulphates, hence it is agreed that its origin is in the HSO_4^- ion. The values of this frequency and its intensity (in parenthesis) in sulphuric acid, nitrosyl sulphate, and solutions of nitrosyl sulphate in sulphuric acid are given in Table I.

It will be seen that whilst the numerical value of the frequency remains practically unaltered the very weak line in the 98 per cent. sulphuric acid is greatly enhanced by the addition of nitrosyl sulphate, and still further enhanced on dilution. It is certain, therefore, that this displacement has its origin in the HSO_4^- ion.

¹² Mulliken and Stevens, *Physic. Rev.*, 1934, 44, 720.

¹³ Foote and Mohler, *Bull. Standards. J. Res.*, 1920—15.5 volts; Boucher, *Physic. Rev.*, 1922, 19, 189—14.0 volts; Smyth, *Proc. Roy. Soc.*, 1923, 105, 116—15.5 volts; Mackay, *Physic. Rev.*, 1924, 24, 319—12.5 volts; Hogness and Lunn, *Physic. Rev.*, 1926, 27, 732—13 volts; Tate and Smith, *Physic. Rev.*, 1932, 39, 270—12.5 volts.

¹⁴ *Proc. Roy. Soc.*, 1935 149A, 327.

¹⁵ *Proc. Roy. Soc. (in the press)*.

TABLE I.

HNSO ₅ (solid).	98 Per Cent. H ₂ SO ₄ .	Solutions of Nitrosyl Sulphate in			
		98 Per Cent.	90 Per Cent.	80 Per Cent.	75 Per Cent. H ₂ SO ₄ .
1045 (4)	1045 (0)	1045 (4)	1041 (5)	1041 (5)	1036 (5)

From the prominence of the HSO₄⁻ ion frequency in nitrosyl sulphate and the identity of the very strong line with a displacement of 2330 cm.⁻¹ in both nitrosyl perchlorate and nitrosyl sulphate it is concluded that nitrosyl sulphate has the ionic configuration [NO⁺][HSO₄⁻].

Further, it can be said that the frequency associated with NO⁺ is about 2330 cm.⁻¹. The observed values for this frequency are tabulated below with their approximate intensities.

TABLE II.

Substance.	(Cm. ⁻¹).	Substance.	(Cm. ⁻¹).
Solid NOHSO ₄	2311 (9)	Solid NOClO ₄	2329 (5)
NOHSO ₄ in		NOClO ₄ in	
98 per cent H ₂ SO ₄	2338 (9)	62 per cent. HClO ₄	2319 (2)
90 " "	2330 (5)	51 " "	2321 (4)
80 " "	2317 (5)	45 " "	2313 (0)
75 " "	2312 (8)	—	—
65 " "	2309 (2)	—	—
60 " "	2305 (1/2)	—	—

The variations in the value of this frequency under different conditions are not very great, and are doubtless associated with variations in the force fields surrounding the molecule. A very fair value is the value of 2330 cm.⁻¹ quoted throughout the paper.

The fundamental frequencies of isoelectronic diatomic molecules of the same type are similar. By comparing the values of the frequencies

TABLE III

Molecule.	Number of Electrons.	ν (cm. ⁻¹) Band Spectra.	ν (cm. ⁻¹) Raman Spectra.
O ₂	16	1556	1555
O ₄ ⁻	15	1860	—
NO	15	1892	—
N ₂	14	2345	2330
NO ⁺	14	—	2311-2338

obtained by band spectra it is observed that the frequencies of NO and O₂⁻ are of the same order of magnitude. The frequency of NO⁺ has not been recorded but, by analogy, should lie close to the observed frequency of N₂. This process of reasoning by analogy is necessitated partly because no Raman data on the vibrational bands of NO exist¹⁶ and partly because such data could not be legitimately compared owing to the differences in the electronic configurations of the two

¹⁶ Rasetti (*Il Nuovo Cim.*, 1930, 7, 261) observed rotational Raman bands only.

molecules, NO and NO⁺. Table III. shows the close similarity in value between N₂ and NO⁺ and indicates that the value suggested for NO⁺ is of the correct order.

Electrolytic Measurements.

In order to substantiate the deductions from Raman measurements electrolytic experiments were undertaken. A qualitative demonstration that nitrosyl sulphate has an ionic structure was made by electrolysing a solution of nitrosyl sulphate in sulphuric acid between a platinum anode and an iron cathode. The lower portion of a glass U-tube was filled with a concentrated solution of nitrosyl sulphate in "Analar" sulphuric acid and the upper portion of each limb filled up with more "Analar" sulphuric acid; electrodes were dipping in the acid. The cell was connected to 220 volt D.C. mains through a 250 ohm resistance and cooled under running water. The iron cathode provided a source of FeSO₄ in the cathode limb where NO⁺ ions would be discharged. After the current had passed for some time, an intense brown colour developed in the cathode limb which suggests that NO⁺ ions are discharged at the cathode and the NO formed in this way combines with the FeSO₄ to give the well-known brown FeSO₄.NO. On reversing the current the brown colour disappeared but re-appeared again in the other limb with diminished intensity after a short time. It is reasonable that the intensity of colour due to FeSO₄.NO should be diminished, since nitrosyl sulphate is not very soluble in sulphuric acid and therefore is probably completely electrolysed by the first passage of current. The experiment shows, however, that, on passing an electric current through nitrosyl sulphate, NO is formed at the cathode and that, therefore, the proposed ionic configuration of the substance is correct.

In further experiments the conductivity of nitrosyl sulphate in nitromethane was quantitatively determined. Hantzsch and Berger² gave values for the conductivity of nitrosyl perchlorate, but stated that the solubility of nitrosyl sulphate in nitromethane was so limited that it was impossible to measure its conductivity. A preliminary experiment showed that the resistance of nitromethane was diminished very greatly by the addition of a few crystals of nitrosyl sulphate, and it was therefore decided to use nitromethane as a solvent in an attempt to determine accurately the conductivity of nitrosyl sulphate. The nitromethane was carefully purified by distillation over phosphoric anhydride and mercuric oxide until its conductivity was 7×10^{-7} ohms⁻¹ at 25° C. The final distillate gave no test for mercury.

Solutions of nitrosyl sulphate in nitromethane ranging from a saturated solution to a solution only 1/16384 saturated were examined. The resistance of the cell filled with pure nitromethane was 95,000 ohms. On dilution, halving the concentration at each stage, the resistance at first increased in the normal manner for a binary electrolyte at relatively high concentrations. At dilutions greater than 1/32 saturated the resistance values did not remain constant after temperature equilibrium had been reached, but fell gradually with time. When the solution was 1/4096 saturated further dilution produced no appreciable change in resistance. These anomalies are almost certainly due to decomposition of the nitrosyl sulphate since a faint odour of NO₂ could be detected.

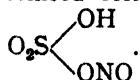
The conductivity of nitrosyl sulphate cannot therefore be determined from measurements in nitromethane solution, but the results obtained do definitely indicate that nitrosyl sulphate is an electrolyte.

Resistance measurements were also made on solution of nitrosyl perchlorate in nitromethane. This substance behaved as a normal electrolyte, the value of the equivalent conductivity approaching a constant value at high dilution. This confirms the observation of Hantzsch and Berger² on this substance.

Conclusions.

Although, unfortunately, quantitative conductivity measurements have not yielded results of high accuracy they have indicated that nitrosyl sulphate and nitrosyl perchlorate are electrolytes. The comparison of frequencies for isoelectronic diatomic molecules, from band spectra and Raman spectra data, has also pointed to the presence of the NO^+ radical in these compounds. The low value of the ionization potential of NO indicates that NO^+ should be easily formed.

No salts of nitrosylsulphuric acid can be isolated although several attempts have been made to do so. This fact also supports the view that the substance is a salt. Actually the salt-like configuration is the ionised form of the structure hitherto accepted by most chemists,



From these facts it follows that NO^+ is a stable radical.

Our best thanks are due to Mr. G. S. Hartley for allowing us to use a set of conductivity apparatus and for giving valuable advice on this part of the work; and to Professor F. G. Donnan for his interest and encouragement.

THE LOSS OF HYDROGEN ATOMS ON WATER-POISONED GLASS SURFACES.

BY W. STEINER.

Received 14th May, 1935.

Consider a mixture of hydrogen atoms and molecules flowing along a glass tube of diameter $2r_0 = 2.5$ cm. with linear velocity $v_z \sim 4$ m./sec. at a pressure $p(z)$, z being the co-ordinate in the direction of the axis of the tube. To suppress wall reactions the surfaces of the tube are poisoned by adding 2.3 to 3.5 per cent. water vapour to the mixture. As pointed out in a previous paper,¹ the principal reaction of the atoms under these conditions is a homogeneous three-body collision, but in addition some atoms diffuse to the walls. From the experimental results given in the same paper it is possible to estimate an *adhesion coefficient* for the atoms on the water-poisoned glass surface of the tube.

Calculation of the Adhesion Coefficient.

Let the concentration of atoms in moles. per cm.³ at the distance of the mean free path λ from the surface of the tube be $[H]_{r_0}$. Then the number of atoms striking the surface per sec., per cm.² is given by

$$vN_L[H]_{r_0} \quad . \quad . \quad . \quad . \quad . \quad (1)$$

If γ is the adhesion coefficient, *i.e.*, the fraction of the impinging atoms which disappears at the surface, then the number of atoms which disappear per sec., per cm.² is

$$\gamma vN_L[H]_{r_0} \quad . \quad . \quad . \quad . \quad . \quad (2)$$

¹ W. Steiner, *Trans. Faraday Soc.*, 1935, **31**, 623.

where v is $1/4$ of the mean thermal velocity of the atoms,² and N_L Loschmidt's number. If M is the molecular-weight, and R the gas-constant

$$\text{then} \quad v = \sqrt{\frac{RT}{2\pi M}} \quad . \quad . \quad . \quad . \quad . \quad (3)$$

In the stationary state the number of atoms consumed by wall-reactions is balanced by the diffusion from the inside of the tube. This transport by diffusion is given in general by $-N_L D \frac{\partial [H]}{\partial r}$. At the wall ($r = r_0$) we have therefore the equation

$$-N_L D \left(\frac{\partial [H]}{\partial r} \right)_{r_0} = \gamma v N_L [H]_{r_0} \quad . \quad . \quad . \quad . \quad (4)$$

and the adhesion coefficient is

$$\gamma = - \frac{D}{v[H]_{r_0}} \left(\frac{\partial [H]}{\partial r} \right)_{r_0} \quad . \quad . \quad . \quad . \quad (5)$$

The balance of the hydrogen atom concentration inside a small volume $d\Omega$ of our tube is given by

$$- \frac{\partial (v_z [H])}{\partial z} = k[H]^2([H] + [H_2]) - D \operatorname{div. grad.} [H] \quad . \quad (6)$$

surplus of the inward flow of atoms = consumption of atoms by reaction (homogeneous) + consumption of atoms by diffusion to the walls.

$$- \frac{\partial (v_z [H])}{\partial z} = k_{\text{exp.}} [H]^2([H] + [H_2]) \quad . \quad . \quad . \quad (7)$$

$k_{\text{exp.}}$ is the three-body-collision constant, which we calculate immediately from the experiments without taking into account the small wall reaction. $k = k_{\text{theor.}}$ is the estimated constant for the unperturbed homogeneous reaction. If we introduce these notations in (6) we get³

$$(k_{\text{exp.}} - k_{\text{theor.}})[H]^2([H] + [H_2]) = -D \operatorname{div grad} [H] \quad . \quad (8)$$

Consider now a small part of our tube of volume

$$V = r_0^2 \pi \Delta z \quad . \quad . \quad . \quad . \quad (9)$$

and with total surface

$$S = 2r_0 \pi \Delta z + 2r_0^2 \pi \quad . \quad . \quad . \quad . \quad (10)$$

We suppose that Δz is so small, that $[H]$ does not change appreciably with z . Then we get from (8) for our volume V the following equation

$$(k_{\text{exp.}} - k_{\text{theor.}}) \iiint [H]^2([H] + [H_2]) dV = -D \iiint \operatorname{div grad} [H] dV \quad (11)$$

We transform the right side of (11) with the help of the theorem of Gauss.

$$-D \iiint \operatorname{div grad} [H] dV = -D \iint \frac{\partial [H]}{\partial n} dS \quad . \quad (12)$$

With

$$dV = r d\phi dr dz \quad . \quad . \quad . \quad . \quad (13)$$

and

$$dS = r_0 d\phi dz \quad . \quad . \quad . \quad . \quad (14)$$

² F. Paneth and K. Herzfeld, *Z. Electrochem*, 1931, **37**, 577.

³ For details of the following calculations, compare¹.

we get

$$(k_{\text{exp.}} - k_{\text{theor.}})2\pi\Delta z \int_0^{r_0} [H]^2([H] + [H_2])rdr = -D2\pi\Delta z \left(\frac{\partial[H]}{\partial r}\right)_{r_0} \quad (15)$$

To calculate the integral on the left side of (15) we assume that $[H]$ is nearly independent of r and therefore constant over the whole cross-section of the tube. Only in the neighbourhood of the surface ($r = r_0$) is $\frac{\partial[H]}{\partial r}$ different from zero. This assumption is valid if the influence of the wall is small. Since in our experiments we do not measure $[H(r, z)]$ but an *average* value

$$[\overline{H(z)}] = \frac{1}{r_0} \int_0^{r_0} [H(r, z)]dr \quad . \quad . \quad . \quad (16)$$

the integral will not be too great if we take this value for our estimate. We get then

$$(k_{\text{exp.}} - k_{\text{theor.}})[H]^2([H] + [H_2])\frac{r_0}{2} = -D\left(\frac{\partial[H]}{\partial r}\right)_{r_0} \quad . \quad (17)$$

and together with (5)

$$\gamma = \frac{[H]^2([H] + [H_2])}{v[H]_{r_0}} \frac{r_0}{2}(k_{\text{exp.}} - k_{\text{theor.}}) \quad . \quad . \quad (18)$$

$k_{\text{exp.}}$, $k_{\text{theor.}}$, $[H]$ and $[H_2]$ we take from our previous paper. We calculate v from (3). From the numerical calculation it will become evident, that $\left(\frac{\partial[H]}{\partial r}\right)_{r_0}$ is very small, therefore $[H]_{r_0}$ is $\sim [H]$ and we get finally

$$\gamma = \frac{r_0}{2v}[H]([H] + [H_2])(k_{\text{exp.}} - k_{\text{theor.}}) \quad . \quad . \quad (19)$$

Numerical Calculations.

In order to estimate numerical values for γ we express the molar-concentrations ³ in percentages c

$$\begin{aligned} [H] &= c \cdot p(z) \times 5.5 \times 10^{-10} \\ [H_2] &= (C - c) \cdot (p(z) \times 5.5 \times 10^{-10}) \\ C &= 100. \end{aligned}$$

Then we get

$$\gamma = \frac{r_0}{2v}c\{(C - c) + c\}(k_{\text{exp.}} - k_{\text{theor.}})p(z)^2 \times (5.5 \times 10^{-10})^2.$$

We have to remember that we can represent the reaction inside the tube by two somewhat different three-body collision reaction constants k'_m and k_m if a *molecule* is the third colliding particle. We have therefore

(1) $k_{\text{exp.}} = k'_m$: small wall reaction and k_a (constant of an *atom* as the third colliding particle) $= \frac{1}{10}k'_m$.

(2) $k_{\text{exp.}} = k_m$: greater wall reaction and $k_a = 0$.

For each of the two values of $k'_{\text{exp.}}$, we estimated

$$k_{\text{theor.}} = 11.0 \times 10^{15} \text{ cm.}^6 \text{ sec.}^{-1} \text{ mole}^{-2}.$$

We get therefore the two corresponding values

$$\gamma' = \frac{r_0}{2v} c \left\{ (100 - c) + \frac{c}{10} \right\} (k_{\text{exp.}} - k'_m) p(z)^2 \times (5.5 \times 10^{-10})^2,$$

and

$$\gamma = \frac{r_0}{2v} c \{ 100 - c \} (k_{\text{exp.}} - k_m) p(z)^2 \times (5.5 \times 10^{-10})^2.$$

The mean values of k'_m and k_m are given in Table I. as well as average c values. This is sufficiently accurate in view of the fact that we can calculate only the order of magnitude.

TABLE I.— $r_0 = 1.25$ CM.; $v = 6.3 \times 10^4$ CM./SEC.; ($T = 300^\circ$ ABS., $M = 1$).

Exp. No.	$p(z)$ mm.	c Per Cent.	$k'_m \times 10^{-15}$	$k_m \times 10^{-15}$	$\gamma' \times 10^6$	$\gamma \times 10^6$
1	0.7	3.6	12.7	13.0	4.0	6.7
2	0.55	4.2	12.1	13.0	2.6	4.5
3 + 4	0.35	3.9	13.2	13.8	3.7	2.2
5 + 6	0.35	7.2	18.0	23.2	3.5	9.0
7 + 8	0.35	6.5	16.6	19.4	3.5	6.7

We see that the adhesion coefficient for hydrogen atoms on the glass surface, poisoned by adding 2.3 to 3.5 per cent water vapour to the flowing mixture of H and H_2 , is

$$\gamma = (2.6 \text{ to } 9) \times 10^{-6}$$

It has this small value only under the conditions mentioned. If the admixture of water vapour is stopped the glass surface becomes more effective, as was evident from other experiments.⁴ If we stopped the flow completely no new water vapour could enter the tube to maintain the right concentration of water (or perhaps O_2 —) molecules on the glass surface, and therefore the wall reaction gradually increased. Immediately after stopping the flow, the hydrogen atoms were transported by diffusion along the tube for more than 1 metre. After ten minutes they were transported for about 30 cm. only. This means that after this short time the wall has become three to four times more effective. It may be that the efficiency of the unpoisoned glass surface is some orders of magnitude greater than that of a poisoned one.

From equation (5) we get the relative decrease of $[H]$ per cm. of the radius of the tube near the surface

$$\left(\frac{\partial [H]}{\partial r} \right)_{r_0} / [H]_{r_0} = - \frac{v \cdot \gamma}{D} \quad (20)$$

with $v = 630$ m/sec, $D \sim 2.1 \times 10^8$ and $\gamma \sim 6 \cdot 10^{-6}$ we have

$$\left(\frac{\partial [H]}{\partial r} \right)_{r_0} / [H]_{r_0} \sim 2 \times 10^{-4}.$$

Therefore we see that, if γ is very small, $[H]$ is practically constant over the whole cross-section of the tube, an assumption which we made in the course of our calculation, and which is now justified.

⁴ W. Steiner und F. W. Wicke, *Z. physik. Chem., Bodenstein Festband*, 1931, 817.

It is interesting to compare the value of γ obtained for hydrogen atoms with the adhesion coefficient on glass surfaces for other atoms and for radicals. For CH_3 and C_2H_5 , γ is notably greater, being nearly 10^{-3} according to Paneth and Herzfeld.² In their experiments a small number of these radicals is carried through a glass tube by a flow of H_2 , N_2 , He or a mixture of $\text{He} + \text{Ne}$ at a pressure of nearly 2 mm. Hg. The condition of the surface must then be dependent on the nature of the flowing gas and the experiments actually suggest that the value of γ depends slightly on the transport gas. For the halogen atoms the value of γ is still greater. This was already evident from the photochemical work on the hydrogen-chlorine and hydrogen-bromine reactions, and has recently been proved more directly.⁵ Schwab and Friess give the value of 4 to 8×10^{-2} for Cl atoms, sinking to 1.3×10^{-2} on adding, to the flowing mixture of Cl_2 and Cl (ca. 15 per cent.), a small amount of methane or chloroform, which seem therefore to poison the wall. For Br atoms practically every collision on the glass surface is effective, according to Schwab.

We hope that a systematic investigation, along the lines which we followed in measuring the recombination of hydrogen atoms, will provide us with the adhesion coefficients for other surface materials under various conditions, and also for other atoms.

Summary.

The adhesion coefficient for hydrogen atoms on a glass surface poisoned by adding 2.3 to 3.5 per cent. water vapour to the flowing mixture of hydrogen atoms and hydrogen molecules is

$$(2.6 \text{ to } 9) \times 10^{-6}.$$

The author is much indebted to Imperial Chemical Industries Limited, through whose kindness this work has been made possible.

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⁵ Rodebusch and Klingelhoefer, *Journ. Americ. Chem. Soc.*, 1933, **55**, 130; Schwab und Freiss, *Z. Elektrochemie*, 1933, **39**, 586; Willey and Foord, *Proc. Roy. Soc. (A)*, 1934, **147**, 309; Schwab, *Z. physik. Chem. (B)*, 1935, **27**, 452.

THE ELECTRON AFFINITY OF THE RADICALS HO_2 AND OH , AND THE OXYGEN MOLECULE.

BY JOSEPH WEISS.

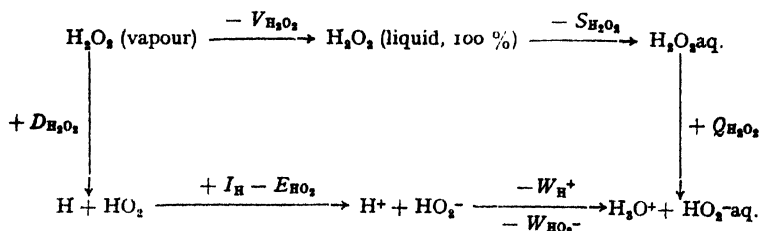
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The electron affinities of the oxygen molecule and the radicals HO_2 and OH play an important rôle in many reactions in the gas phase and in solution. No values have previously been published. Although the experimental data available are not quite sufficient to enable accurate evaluation to be made, it is possible by employing a few reasonable assumptions to estimate them with some certainty.

The Electron Affinity of the HO_2 Radical.

The electron affinity of the HO_2 radical can be derived from the following cycle. We condense H_2O_2 vapour to liquid (100 per cent.) H_2O_2 by removing the heat of evaporation ($V_{\text{H}_2\text{O}_2}$) and then dissolve the liquid hydrogen peroxide in an excess of water by removing the heat of solution ($S_{\text{H}_2\text{O}_2}$). Finally, we dissociate the dissolved H_2O_2 into H_3O^+ and HO_2^- aq. ions by supplying the heat of electrolytic dissociation ($Q_{\text{H}_2\text{O}_2}$).

Alternatively, we can dissociate the H_2O_2 vapour into H atom and HO_2 radical (heat of dissociation $D_{\text{H}_2\text{O}_2}$). We then ionise the H-atom (ionisation potential I_{H}) and transfer the electron to the HO_2 radical (electron affinity E_{HO_2}). Finally, these ions can be dissolved by removing their heats of hydration ($W_{\text{H}_3\text{O}^+}$, $W_{\text{HO}_2^-}$). The cycle process is thus represented by the following scheme:—



We therefore obtain the equations:

$$-V_{\text{H}_2\text{O}_2} - S_{\text{H}_2\text{O}_2} + Q_{\text{H}_2\text{O}_2} = +D_{\text{H}_2\text{O}_2} + I_{\text{H}} - E_{\text{HO}_2} - W_{\text{H}^+} - W_{\text{HO}_2^-} \quad (1)$$

$$-0.50 - 0.44 + 0.37 = +4.08 + 13.6 - E_{\text{HO}_2} - 10.9 - 2.4$$

The numerical values in electron volts (per mol.) are given below. $V_{\text{H}_2\text{O}_2}$ is taken from the work of Maass and Hiebert.¹ $S_{\text{H}_2\text{O}_2}$ has been measured by Matheson and Maass,² and also by Roth, Grau and Meichsner.³ $Q_{\text{H}_2\text{O}_2}$ has been obtained by Joyner⁴ from direct measurements and from the temperature coefficient of the dissociation constant. The dissociation energy ($D_{\text{H}_2\text{O}_2}$) of H_2O_2 into HO_2 radical and H atom has been discussed in a previous paper.⁵ I_{H} and $W_{\text{H}_3\text{O}^+}$ are given their accepted values.⁶

Some assumption must be made to obtain the heat of hydration of the HO_2^- ion. The heat of hydration is mainly governed by the radius of the ion and its charge.⁶ One would expect the radius of the HO_2^- ion to be somewhat greater than that of the O_2 molecule. The largest monovalent negative ion whose heat of hydration is known is the I^- ion, for which this value is 2.65 electron volts. Its radius may be less than that of the HO_2^- ion, and therefore we have taken the heat of hydration of the latter ion to be lower than that of the iodine ion, namely 2.4 electron volts.

We finally obtain the value of $E_{\text{HO}_2} \sim 4.6$ electron volts for the electron affinity of the HO_2 radical in the gas phase.

¹ O. Maass and P. G. Hiebert, *J. Amer. Chem. Soc.*, 1924, **46**, 2699.

² G. L. Matheson and O. Maass, *ibid.*, 1929, **51**, 683.

³ Roth, Grau and Meichsner, *Z. anorg. Chem.*, 1930, **193**, 166.

⁴ Joyner, *ibid.*, 1912, **77**, 103.

⁵ J. Weiss, *Trans. Faraday Soc.*, 1935, **31**, 669. In connection with this paper I would like to mention that the radical HO_2 , assumed by Haber, had already been proposed some years ago by H. S. Taylor, *Z. physik. Chem.*, 1926, **120**, 183.

⁶ Cf. Landolt-Börnstein, *Physik. Chem. Tabellen*; K. F. Herzfeld, *Kinetische Theorie der Wärme*. (Vieweg, 1926).

The Electron Affinity of the OH Radical.

We condense water vapour to liquid water by removing the heat of evaporation ($V_{\text{H}_2\text{O}}$) and then dissociate the water into its ions H_3O^+ aq. and OH^- aq. by supplying the heat of electrolytic dissociation ($Q_{\text{H}_2\text{O}}$).

Alternatively, we can dissociate into H atoms and OH radicals in the gas phase ($D_{\text{H}_2\text{O}}$), effect the electron transfer, and finally dissolve the ions in water and allow them to hydrate. We thus obtain the following equation (with the same notation as above):—

$$-V_{\text{H}_2\text{O}} + Q_{\text{H}_2\text{O}} = D_{\text{H}_2\text{O}} + I_{\text{H}} - E_{\text{OH}} - W_{\text{H}^+} - W_{\text{OH}^-} \quad (2)$$

$$-0.46 + 0.6 = +5.0 + 13.6 - E_{\text{OH}} - 10.9 - 3.8$$

All values, except the heats of hydration, are known with considerable accuracy.

W_{H^+} is given the same value as above, and W_{OH^-} is taken from van Arkel and der Boer.⁷

We obtain the value of $E_{\text{OH}} \sim 3.7$ electron volts for the electron affinity of the OH radical in the gas phase.

The Electron Affinity of the O_2 Molecule.

The electron affinity can be calculated by a similar cycle. Starting with HO_2 in the gas phase, we can (a) dissolve in water and ionise in H_3O^+ and O_2^- aq., or alternatively (b) dissociate in H atom and O_2 molecule in the gas phase, effect the electron transfer, and finally dissolve the ions in water and allow them to hydrate. We thus obtain the following equation (with the same notation as above):—

$$S_{\text{HO}_2}^{(\text{v})} + Q_{\text{HO}_2} = D_{\text{HO}_2} + I_{\text{H}} - E_{\text{O}_2} - W_{\text{H}^+} - W_{\text{O}_2^-} \quad (3)$$

$$-0.5 + 0.02 = +1.95 + 13.6 - E_{\text{O}_2} - 10.9 - 2.40$$

In this case, further assumptions are necessary. The heat of solution of HO_2 vapour ($S_{\text{HO}_2}^{(\text{v})}$) in water should be of the same order of magnitude as that of H_2O_2 vapour. In both cases this energy is mainly governed by the interaction of dipoles, and the unsaturated character of the HO_2 radical will not be of appreciable influence, particularly since the solvent molecules themselves are saturated. Further, the heat of hydration of the O_2^- ion will approximate to that of the HO_2^- ion, since their radii will not differ greatly. The value of the dissociation energy (D_{HO_2}) has been given in a previous paper.⁵ Finally, we require the heat of electrolytic dissociation of HO_2 in water. No experimental data are available, but it can be estimated by comparison with the very similar ionisation of H_2O_2 . As the *a priori* probabilities (and specific heat terms) cannot differ greatly, we can calculate the heat of ionisation of HO_2 from known values of the ionisation constants of H_2O_2 and HO_2 ($K_{\text{H}_2\text{O}_2}$ and K_{HO_2}) and the known heat of ionisation of H_2O_2 ($Q_{\text{H}_2\text{O}_2}$). We have the equation:—

$$\log \frac{K_{\text{H}_2\text{O}_2}}{K_{\text{HO}_2}} = \frac{Q_{\text{HO}_2} - Q_{\text{H}_2\text{O}_2}}{2.3 RT} \quad (4)$$

From recent experiments⁸ on the effect of the H^+ ion concentration on the catalytic decomposition of hydrogen peroxide, we are able to

⁷ van Arkel and de Boer, *Die chemische Bildung als elektrostatische Erscheinung*. (Hirzel, 1931).

⁸ Will be published shortly; see also G. Kornfeld, *Z. physik. Chem.* (in the press).

calculate the dissociation constant in water which has a value of approximately $K_{\text{HO}_2} \sim 10^{-6}$ (20° C.). This gives the value $Q_{\text{HO}_2} = 0.02$ electron volts from equation (4).

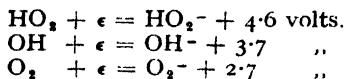
We thus get for the electron affinity of the oxygen molecule in the gas phase

$$E_{\text{O}_2} \sim 2.7 \text{ electron volts.}$$

It may be mentioned that Bradbury⁹ obtained a value of 1.6 electron volts from the study of the interaction between the O_2 molecule in the gas phase and low voltage electrons. However, it is very probable that his figure refers to the excited (metastable) level of the O_2 molecule at 1.62 volts.

Summary.

The electron affinities of the HO_2 and OH radicals and the O_2 molecule in the gas phase have been calculated from cyclic processes. The values obtained (in electron volts) are:—



I would like to thank Dr. E. Teller and Dr. E. Rabinowitch for many valuable discussions, and Professor F. G. Donnan, F.R.S., for his great interest in this work.

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⁹ Bradbury, *Physik. Rev.*, 1933, 44.

THE KINETICS OF POLYMERISATION PROCESSES.

BY G. GEE AND ERIC K. RIDEAL.

Received 17th May, 1935.

The study of the kinetics of processes of polymerisation has been largely neglected. Two opposing tendencies with respect to the classification of polymerisation reactions may be observed: Carothers¹ has pointed out the essential unity of the whole field, whereas Chalmers² prefers to consider a number of divisions which seem at first sight a little arbitrary. It is suggested that the mechanism which is proposed below may serve to show the relationship between polymerisation processes whose kinetics are outwardly very different.

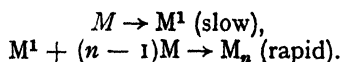
Chalmers has discussed the two principal mechanisms which have been advanced to account for the observed facts of polymerisation, namely

¹ Carothers, *Chem. Rev.*, 1931, 8, 378; *J.A.C.S.*, 1929 onwards.

² Chalmers, *J.A.C.S.*, 1934, 56, 912; *Can. J. Res.*, 1932, 7, 113.

the "Stepwise" and polymerisation chain processes. It is, of course, sufficiently clear that the former cannot, without physically improbable assumptions, lead to polymers of long chain length, and it seems to be now generally accepted³ that any true polymerisation—giving products more than two units long—proceeds by a chain mechanism. Such cases as the dimerisation of ethylene studied by Pease⁴ must be recognised as exceptions to this generalisation.

No complete analysis of the kinetics of a polymerisation chain has been made, although it has been pointed out by Semenoff,⁵ Chalmers and others, that if the chain consists of a slow activation of the initial material followed by a rapid reaction of the active body with a series of monomers, the reaction will be pseudo unimolecular.



The total velocity is then $-\frac{dx}{dt} = knx$ where k is the velocity constant of the first reaction. It is necessary, however, to assume that the chain length of the reaction is constant and independent of the extent of the reaction, while no mechanism is proposed by which the chains are stopped. Whilst the data for the kinetics of polymerisation are extremely scanty, Chalmers has shown that a number of measurements made by Whitby⁶ and others are approximately in accord with a unimolecular law. This, however, is by no means a general rule, and induction periods are very frequently observed, the reaction showing superficial resemblances to an autocatalytic one. A study of polymerisation processes in surface films^{6a} seems to show that the induction period is to be regarded as quite a fundamental property, and leads to the conclusion that the point at which the reaction velocity becomes a maximum depends upon the size of the polymer, occurring nearer the start of the reaction as the complexity increases.

The assumption of constancy of chain length which has always been made in deriving the unimolecular law for polymerisation is scarcely justified by the published data, and is in fact almost certainly erroneous. Staudinger⁷ and Houtz and Adkins⁸ have found that while the polymers appearing near the beginning of the reaction may be already very complex, at its termination they are still more so, while Whitby and Katz⁶ have shown further that at a given stage the product obtained in the polymerisation of indene was far from homogeneous. Several mechanisms can be advanced for the stopping of the chains in polymerisation reactions, apart from the specific effects of extraneous materials acting as inhibitors, or the walls serving as chain breakers. Taylor and Vernon⁹ have suggested that the heat of combination of the active molecule with a monomer provides the energy for reaction of the dimer with another monomer, and the process continues until the energy of the group is too small for further reaction, loss of energy being supposed to occur either as above (by deactivation) or by distribution of the energy over the

³ Compare, e.g. refs. 2, 5, 9, 12.

⁴ Pease, *J.A.C.S.*, 1930, **52**, 1160; 1931, **53**, 613.

⁵ Semenoff, *Chemical Kinetics and Chain Reactions*, p. 444.

⁶ Whitby, *J.A.C.S.*, 1928, **50**, 1160; *Can. J. Res.*, 1931, **4**, 487; 1932, **6**, 204.

^{6a} *In press*.

⁷ Staudinger, *Ber.*, 1929, **62**, 245.

⁸ Houtz and Adkins, *J.A.C.S.*, 1933, **55**, 1617.

⁹ Taylor and Vernon, *ibid.*, 1931, **53**, 2527.

whole aggregate; but it is difficult to understand the mechanism by which long chains could be built up if this redistribution of energy among the squared terms actually occurred. Another possible mechanism suggests, *e.g.* in styrene, that long polymers are in themselves unstable and that the chain length obtained is the result of an equilibrium between decomposition and polymerisation reactions. Finally, it may be suggested that the growth or termination of a chain on collision with a monomer is dependent on two factors: the steric factor and the energy of activation. If, as appears to be the case in a number of polymerisation reactions, the terminal reactive group is still active at the end of relatively long chains (*e.g.* 100 molecules) it is doubtful whether the energy of activation varies much with chain length; for any variation due to distribution of energy among the squared terms would have been noticeable in the early stages of chain formation. It seems more probable that in many cases the steric factor becomes increasingly important. In the case of certain polymerisations the possibility of the chain being either stopped or propagated by two specific and distinct types of collision has already been examined by Melville and Rideal¹⁰ and found to hold in the case of the condensation of acetylene.

The Induction Period.

Before proceeding to an analysis of the problem of the importance of the steric factor in polymerisation chains, another method of approach may be considered. It has already been mentioned that polymerisations frequently approximate to an autocatalytic path, and that the induction period is perhaps to be regarded as an essential feature. The phenomenon of the induction period has been discussed from the point of view of the thermal gaseous chain reaction by Semenoff,¹¹ who proposed as a general equation relating the fraction of the initial material which had undergone reaction with the time measured from the time of half reaction:

$$\xi = \frac{1}{1 + e^{-\phi\tau}} \quad (1)$$

where ϕ is a function of pressure and temperature of the form:

$$\phi = \beta p^m e^{-E/RT} \quad (2)$$

If in these equations we replace ϕ by k_s and τ by $t - t_{\frac{1}{2}}$, where $t_{\frac{1}{2}}$ is the time of half reaction, we readily find:

$$\frac{d\xi}{dt} = k_s \xi (1 - \xi) \quad (3)$$

which clearly requires a parabolic curve for a plot of $\frac{d\xi}{dt}$ against ξ . Equation (3) can be expressed in terms of any parameter χ which varies linearly with ξ . If χ_0 , χ_∞ , and χ be the values of this parameter at the start of the reaction, at the end, and at time t , it is easily seen that:

$$\frac{d\chi}{dt} = \frac{k_s}{\chi_\infty - \chi_0} (\chi_\infty - \chi)(\chi - \chi_0) \quad (4)$$

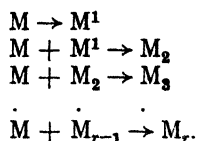
We shall discuss later the relationship between this equation and others derived from a material chain mechanism.

¹⁰ Rideal, *P.R.S.A.*, 1934, 146, 268.

¹¹ Semenoff, *Z. physik. Chem.*, 1931, 11B, 464; *Physik. Z. der Sowjet*, 1933, 4, 906.

Kinetics of a Polymerisation Chain.

We shall consider a chain initiated by the activation of monomer molecules, and propagated by the union of successive monomers with the active molecule the growing polymer, which we shall suppose to retain the original energy of activation.* If we denote the monomer by M , the active form by M^1 and the polymer containing r units by M_r , we shall have :



The velocity constants $k_1, k_2, k_3 \dots k_r \dots$ of these stages fall into two classes: from k_2 onwards all are of similar type and, for reasons stated above, may be considered to change progressively by a steric factor. We shall return later to discuss the effect of varying the factor actually chosen; for the present, k_{r+1} can be expressed in terms of a parameter K by the equation

$$k_{r+1} = \frac{K}{r} \quad \dots \quad (5)$$

k_1 is unique but may be included in the general scheme by writing

$$k_1 = K\alpha n_0 \quad \dots \quad (6)$$

where n_0 is the number of molecules of M initially present, and is inserted in equation (6) in order to make the dimensions correct while leaving α as a pure number, the value of which will clearly determine the properties of the system.

Let the numbers of molecules of the various species $M, M^1, M_2 \dots M_r$ be $n_1, n^1, n_2 \dots n_r$. It will be convenient to reckon these numbers in terms of the monomer, so that we have always :

$$n_0 = n_1 + n^1 + n_2 + n_3 + \dots + n_r + \dots \quad (7)$$

We have now to select a suitable parameter in terms of which the kinetics are to be expressed, and the most generally useful would seem to be the total number of molecules N , reckoned this time in terms of complete molecules, giving

$$N = n_1 + n^1 + \frac{1}{2}n_2 + \frac{1}{3}n_3 + \dots + \frac{1}{r}n_r + \dots \quad (8)$$

For the case of polymerisation in the gas phase N will be directly measured by the pressure, so long as the products remain gaseous; while for reactions followed by cryoscopic⁹ or ebullioscopic measurements N is also given directly by the experimental data. Whitby's measurements refer to the fraction polymerised, which is simply related to N , but the dilatometric method employed by Starkweather and Taylor¹² requires a further assumption. An analogous problem is discussed elsewhere in the paper already referred to.^{8a}

A further quantity ν may be introduced, as the mean chain length of

* Possibly the terminal group in the growing polymer may be transformed by the energy of activation into a stable isomeric form requiring a negligibly small energy of activation for subsequent reaction.

¹² Starkweather and Taylor, *J.A.C.S.*, 1930, **52**, 4708.

the portion which has polymerised. It follows from equations (7) and (8) that :

$$\frac{1}{2}n_2 + \frac{1}{3}n_3 + \dots + \frac{1}{r}n_r = \frac{n_0 - n_1 - n^1}{\nu} = N - n_1 - n^1 \quad (9)$$

For a first approximation, the concentration n^1 of the active monomer may be neglected, whence from (9)

$$n_1 = \frac{N\nu - n_0}{\nu - 1} \quad . \quad . \quad . \quad . \quad (10)$$

We have :

$$\frac{dN}{dt} = \frac{dn_1}{dt} + \frac{dn^1}{dt} + \frac{1}{2}\frac{dn_2}{dt} + \frac{1}{3}\frac{dn_3}{dt} + \dots + \frac{1}{r}\frac{dn_r}{dt} + \dots \quad (11)$$

and

$$\left. \begin{aligned} -\frac{dn_1}{dt} &= Kn_1\left(\alpha n_0 + n^1 + \frac{1}{2}n_2 + \frac{1}{3}n_3 \dots + \frac{1}{r}n_r + \dots\right) \\ \frac{dn_1}{dt} &= Kn_1(\alpha n_0 - n^1) \\ \frac{dn_2}{dt} &= 2Kn_1(n^1 - \frac{1}{2}n_2) \\ &\vdots \\ \frac{dn_r}{dt} &= rKn_1\left(\frac{n_{r-1}}{r-1} - \frac{n_r}{r}\right) \end{aligned} \right\} \quad (12)$$

Combining (11) and (12)

$$\begin{aligned} -\frac{dN}{dt} &= Kn_1\left(n^1 + \frac{1}{2}n_2 + \frac{1}{3}n_3 + \dots + \frac{1}{r}n_r + \dots\right) \\ -\frac{dN}{dt} &= Kn_1(N - n_1) \quad . \quad . \quad . \quad . \quad (13) \end{aligned}$$

Combining with (10), this gives :—

$$-\frac{dN}{dt} = \frac{K}{\nu} n_1(n_0 - n_1) \quad . \quad . \quad . \quad . \quad (14a)$$

$$-\frac{dN}{dt} = \frac{K}{(\nu - 1)^2}(n_0 - N)(N\nu - n_0) \quad . \quad . \quad (14b)$$

These equations do not yet give the complete variation of N , since ν is itself a function of t . If, however, we suppose the conditions to be such that ν is substantially constant throughout the course of the reaction, we can easily see that the equation reduces to the same form as (4). If we denote values at the end of the reaction by a subscript ∞ , we have

$$N_\infty \nu_\infty = n_0 \quad . \quad . \quad . \quad . \quad (15)$$

Now if ν were constant during the reaction ν would be equal to ν_∞ and (14b) would reduce to

$$-\frac{dN}{dt} = \frac{K\nu_\infty}{(\nu_\infty - 1)^2}(n_0 - N)(N - N_\infty) \quad . \quad . \quad (16)$$

Since the initial value of N is n_0 , this is precisely equivalent to equation (4). The condition for what we may term the "Semenoff" form of

curve is thus that the chain length of the polymer shall remain constant during the reaction: in practice this condition will be approached by short chain processes for which α is large, or the steric factor (or other possible cause) gives a very rapid decrease of k_r with increasing polymer size. This represents, then, one extreme type of curve which may be found in practice: the other extreme is obtained by considering the case when α is small, and continuing to neglect n^1 , when we can find an approximate relationship between ν and N .

Neglecting n^1 in equation (9), and differentiating with respect to n_1 , we have:

$$\frac{-\nu - (n_0 - n_1) \frac{d\nu}{dn_1}}{\nu^2} = \frac{Kn_1}{\frac{dn_1}{dt}} \cdot \frac{d}{dt} [n^1 - \frac{1}{2}n_2 + \frac{1}{2}n_2 - \frac{1}{3}n_3 + \frac{1}{3}n_3 - \frac{1}{4}n_4 + \dots]$$

$\rightarrow 0$ if n^1 be neglected.

$$\therefore \frac{d\nu}{dn_1} = \frac{-\nu}{n_0 - n_1} \quad (17)$$

whence

$$\frac{\nu}{\nu_\infty} = \frac{n_0 - n_1}{n_0} \quad (18)$$

Combining equations (10), (14b), (15) and (18), it follows at once that

$$-\frac{dN}{dt} = KN_\infty(N - N_\infty) \quad (19)$$

For small values of α —which evidently means long chains—the velocity equation thus reduces to the unimolecular form which has been frequently reported.

The problem of the transition between the two extreme forms of curve may be treated most simply by deriving the condition for $\frac{dN}{dt}$ to become a maximum. By further differentiation it is easily shown that

$$\frac{d^2N}{dt^2} = \frac{K^2}{\nu} n_1(n_0 - n_1) \left\{ \alpha n_0 + \frac{n_0 - n_1}{\nu} \right\} - \alpha K^2 n_1^2 n_0 \quad (20)$$

For a maximum of $\frac{dN}{dt}$ this must vanish, whence

$$\alpha n_1 n_0 = \frac{n_0 - n_1}{\nu} \left\{ \alpha n_0 + \frac{n_0 - n_1}{\nu} \right\} \quad (21)$$

If α is small enough to be completely neglected, this reduces at once to

$$\left(\frac{n_1}{n_0} \right)_{\max.} = 1 \quad (22)$$

as we should anticipate from equation (19).

A better approximation results from neglecting α as an additive term only, whence

$$n_1^2 - (2 + \alpha\nu^2)n_0n_1 + n_0^2 = 0, \text{ and} \\ \left(\frac{n_1}{n_0} \right)_{\max.} = 1 - \frac{1}{2}\alpha\nu^2 \left\{ \sqrt{\frac{4}{\alpha\nu^2} + 1} - 1 \right\} \quad (23)$$

in which ν is to be given its value at this stage of the reaction. We know that at the start of the reaction $\nu = 2$, since only dimer is present.

For long chain processes (α small) the maximum occurs nearly at the start of the reaction, while for short chain processes the value of ν attained is never very large. The effect of α on the point at which the maximum occurs has, therefore, been calculated for $\nu = 2$

TABLE I.—POSITION OF MAXIMUM VELOCITY.

α .	$\nu = 2$.		$\nu = 3$	
	$(\frac{n_1}{n_0})_{\max.}$	$(\frac{N}{n_0})_{\max.}$	$(\frac{n_1}{n_0})_{\max.}$	$(\frac{N}{n_0})_{\max.}$
0.1	0.54	0.77	0.40	0.60
0.01	0.82	0.91	0.74	0.83
0.001	0.94	0.97	0.91	0.94
0	1.00	1.00	1.00	1.00

and $\nu = 3$, with various values of α , the results being tabulated.

We thus arrive at a view of the "velocity" curve ($\frac{dN}{dt} \sim N$) which for short chain processes is nearly parabolic, becoming with increasing chain length (decreasing α) more and more asymmetrical until the primary

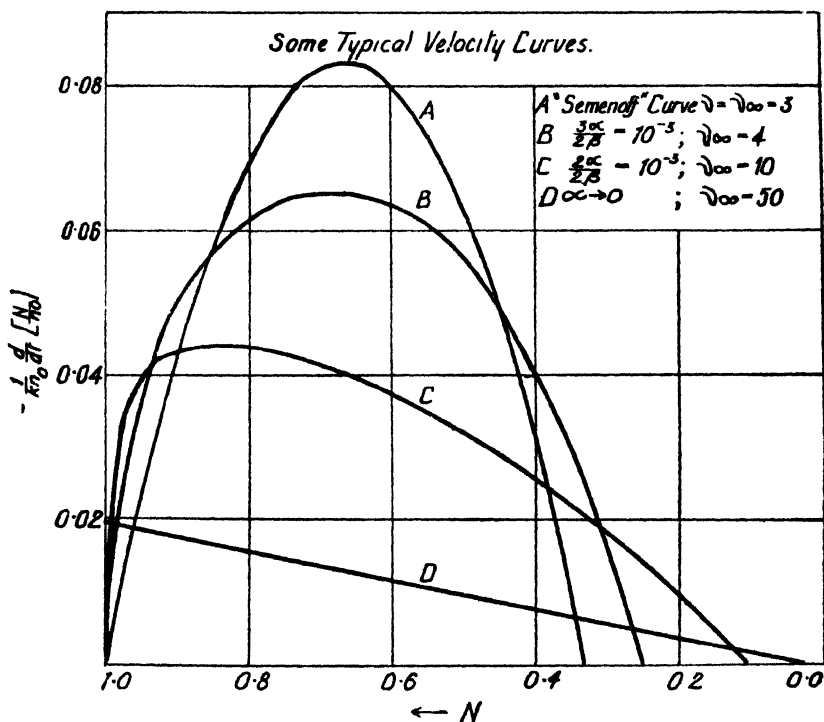


FIG. 1.

induction period finally becomes too short to be measured and the process degenerates into a pseudo-unimolecular form. A set of such curves is shown in Fig. 1.*

* Curves B and C are based on the $(\bar{\nu}_i - \xi)$ relationship given by equation (31) below.

The specific constants α and (Kn_0) of the process may be obtained from suitable experimental data in the following way: It has already been pointed out that at the start of the reaction $\nu = 2$, and inserting this value in equation (14b) we have

$$-\left(\frac{dN}{dt}\right)_{\nu=2} = K(n_0 - N)(2N - n_0) \\ \cong K(n_0 - N)n_0,$$

since initially $N = n_0$,

$$\therefore \frac{d}{dN}\left(\frac{dN}{dt}\right)_{\nu=2} = Kn_0 \quad . \quad . \quad . \quad (24)$$

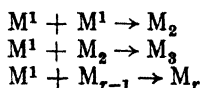
The initial slope of the "velocity" curve therefore measures Kn_0 directly. In a similar way, from equation (20) we can see that the initial value of $\frac{d^2N}{dt^2}$ is

$$\left(\frac{d^2N}{dt^2}\right)_{t \rightarrow 0} = -\alpha K^2 n_0^3 \quad . \quad . \quad . \quad (25)$$

whence α may be found.

Variation of Polymer Size during Reaction.

The equation (18) which has been developed above for the variation of chain length during the reaction is clearly only an approximation, since it leads to the meaningless value of $\nu = 0$ at the start of the reaction. It has not been found possible to obtain a completely satisfactory equation, but a better approximation results from taking account of the concentration of the active monomer. In order to do this, it is necessary to modify somewhat the reaction mechanism considered, since it will be evident on inspection that we have so far provided no means whereby the active monomer can disappear except by reaction with monomer, so that a quantity of it would remain finally. We clearly have the possibility of a further series of reactions



Although, as has been shown by Ouellet¹³ in the case of the oxidation of phosphorus, such reactions produce only a second order effect, they must actually be present and will, in fact, be partly responsible for finally reducing the concentration of M^1 to zero. If we suppose the rate of a reaction involving M^1 to be β times that of a similar reaction of M , the complete equation for $\frac{dn_r}{dt}$ becomes:

$$\frac{dn_r}{dt} = rK(n_1 + \beta n^1)\left(\frac{n_{r-1}}{r-1} - \frac{n_r}{r}\right) \quad . \quad . \quad (26)$$

Since we are now going to correct for the concentration n^1 we evaluate it by putting $\frac{dn^1}{dt} = 0$, or

$$\frac{dn^1}{dt} = Kn_1(\alpha n_0 - n^1) - \beta Kn^1\left(n^1 + \frac{1}{2}n_2 \dots + \frac{1}{r}n_r + \dots\right) = 0 \quad (27)$$

¹³ Ouellet, *Trans. Faraday Soc.*, 1933, **29**, 486.

This gives, as a good approximation,

$$n^1 = \frac{\alpha v n_1 n_0}{\beta(n_0 - n_1)} \quad (28)$$

It is clear that n^1 is small enough to be neglected except when it occurs alone, and it is easily shown that equations (14, a, b) take the same form as before. In deriving (18) it was, however, necessary to neglect n^1 when it occurred alone: if now we make the approximation of equation (28) we find that, provided α is not too large,

$$v + (n_0 - n_1) \frac{dv}{dn_1} = \frac{\alpha v^4 n_1 n_0}{\beta(n_0 - n_1)^2} \quad (29)$$

The solution of this equation, putting in $v = v_\infty$ when $n_1 = 0$ is

$$\frac{1}{v^3} = \frac{1}{v_\infty^3} + \frac{3\alpha n_0 n_1}{2\beta(n_0 - n_1)^2} \quad (30)$$

or writing ξ as before as the fraction polymerised:

$$\frac{1}{v^3} = \frac{1}{v_\infty^3} + \frac{3\alpha(1 - \xi)}{2\beta\xi^2} \quad (31)$$

Some typical curves given by this equation are plotted in Fig. 2, which represents the variation of v with ξ . It is evident that there is a value of α/β for any given v_∞ which makes the curve nearly linear, while decreasing either α/β or v_∞ gives a curve in which v_∞ is closely approached for quite small values of ξ . In drawing these curves α/β and v_∞ have been treated as independent variables, as no method has yet been found of

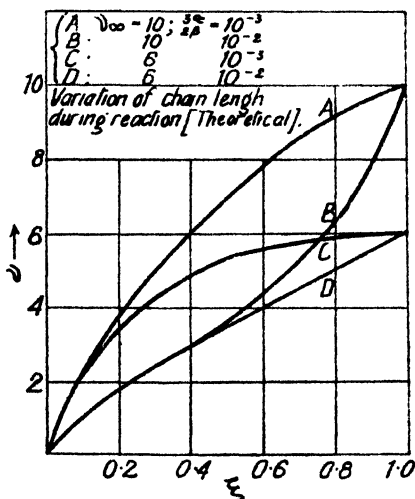


FIG. 2.

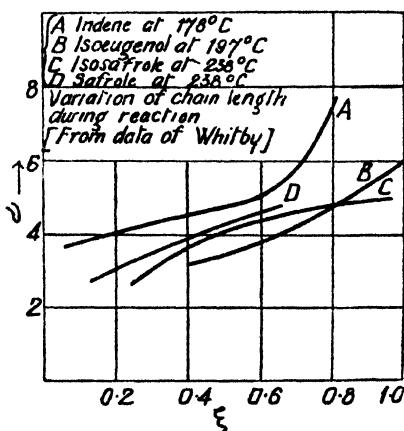


FIG. 3.

deriving the theoretical relationship between them. The curves obtained may be compared with those of Fig. 3, which are drawn from the data of Whitby. In view of the fact that molecular weights of the polymer were obtained by Whitby from cryoscopic data, the probable accuracy is not high, and no consistent form of curve is shown. Nevertheless, we can conclude that the analysis which has been presented gives an increase

in complexity which is comparable with that which is actually observed, and that it is capable of giving approximately the right kind of variation. The equations given clearly break down at the very beginning of the reaction, *i.e.* for very small values of ξ , and fail to give the correct limit of $\nu = 2$ at $\xi = 0$.

Consideration of other Steric Factors.

So far we have considered only a steric factor represented by the law $k_{r+1} = \frac{K}{r}$: we shall now proceed to discuss what variations are introduced when other steric factors are employed. The problem can best be dealt with by giving briefly the results of a similar analysis, based on the alternative law:

$$k_{r+1} = \frac{K}{r^2} \quad . \quad . \quad . \quad . \quad (32)$$

In carrying out this analysis, it is necessary to approximate to the value of the series

$$\frac{1}{4}n_2 + \frac{1}{8}n_3 + \dots + \frac{1}{r^2}n_r + \dots$$

If $\bar{\nu}$ is the root mean square value of the chain length of the fraction polymerised, we have

$$\frac{1}{4}n_2 + \frac{1}{8}n_3 + \dots + \frac{1}{r^2}n_r + \dots = \frac{n_0 - n_1 - n'}{\bar{\nu}^2} \quad . \quad (33)$$

Neglecting n' , and making the approximation of writing $\nu = \bar{\nu}$, this becomes:

$$\frac{1}{4}n_2 + \frac{1}{8}n_3 + \dots + \frac{1}{r^2}n_r + \dots = \frac{n_0 - n_1}{\nu^2} \quad . \quad (34)$$

On this basis, it is easily shown that

$$-\frac{dN}{dt} = \frac{K}{\nu(\nu-1)^2}(N\nu - n_0)(n_0 - N) \quad . \quad . \quad (35)$$

which differs from (14b) by a factor $1/\nu$. The condition for this to reduce to the "Semenoff" parabolic form is given, as before, by $\nu \cong \nu_\infty$.

The solution of the problem is formally quite similar to that obtained before. From the limiting "Semenoff" form the velocity curve degenerates as α is decreased until for small α a unimolecular law is obeyed. The characteristic constants (Kn_0) and α are given, as in the previous case, by the initial values of $\frac{d}{dN}\left(\frac{dN}{dt}\right)$ and $\frac{d^2N}{dt^2}$.

$$\frac{d}{dN}\left(\frac{dN}{dt}\right)_{\nu=2} = \frac{1}{2}Kn_0 \quad . \quad . \quad . \quad (36)$$

$$\left(\frac{d^2N}{dt^2}\right)_{t \rightarrow 0} = -\alpha K^2 n_0^3 \quad . \quad . \quad . \quad (37)$$

The equations analogous to (29) and (31) for the variation of chain length during the reaction are found to be:

$$\nu + (n_0 - n_1) \frac{d\nu}{dn_1} = \frac{\alpha n_1 n_0 \nu^6}{\beta(n_0 - n_1)^2} \quad . \quad . \quad . \quad (38)$$

and

$$\frac{1}{\nu^6} = \frac{1}{\nu_\infty^6} + \frac{5\alpha}{12\beta} \left\{ 1 + \frac{4}{\xi^2} - \frac{3}{\xi} \right\} \quad . \quad . \quad . \quad (39)$$

Some typical plots of ν against ξ , as calculated with the aid of equation (39) are given in Fig. 4. In order to facilitate comparisons, it may be noted that curve E of Fig. 4 is calculated from the same constants (α/β and ν_∞) as curve C of Fig. 2. As before, we have no relationship between α/β and ν_∞ , but it appears fairly evident on physical grounds that with the larger steric factor the major increase in chain length will occur during the early stages of the reaction, so that the $\nu - \xi$ curve will tend to be concave downwards. Now it is easily seen that in order to obtain curves of this shape for large values of ν_∞ it will be necessary to take very small values of α/β : that is to say, extremely slow reactions are needed. A smaller steric factor, such as was first considered ($1/\nu$) thus appears to be much more probable in the case of polymerisations leading to products of high complexity, while conversely it is clear that a large steric factor would necessarily cause the polymerisation chains to be short.

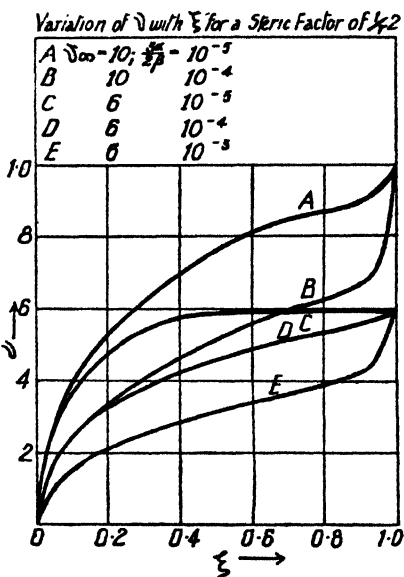


FIG. 4.

Our thanks are due to the Imperial Chemical Industries Dyestuffs Group for a grant in aid to one of us (G. G.) which rendered this work possible.

Summary.

The kinetics of a polymerisation chain are discussed, and evidence is presented for the view that a steric factor provides a sufficient mechanism for chain termination. The period of induction which is frequently observed is regarded as a fundamental property, the point of maximum reaction velocity depending on the chain length. For long chains, the maximum occurs early, and the curve degenerates into a pseudo unimolecular form. For a hypothetical case in which the chain length is constant throughout the reaction, the velocity equation takes the form proposed by Semenov for thermal gaseous chain reactions. In practice this condition is approached by very short chains and/or a large steric factor.

The variation of chain length during the reaction is examined, and the theoretical curves compared with published data.

Changing the steric factor does not affect the main conclusions, but with a large steric factor the chains must always be fairly short.

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SOME ASPECTS OF THE EQUATION OF STATE OF MONOLAYERS.

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Communicated by Eric K. Rideal.

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The applicability of the kinetic theory to monolayers of insoluble substances was suggested by the early observations of Traube,¹ and has now gained general acceptance from the work of Langmuir,² Schofield and Rideal,³ and Adam and Jessop.⁴ It is now apparent that solid films require explanation in terms of lattice theory,⁵ and that liquid condensed films and the liquid expanded films explained by Langmuir⁶ as having a "duplex" structure, must await an adequate theory of liquids before satisfactory interpretation. For imperfect gaseous and vapour films a number of semi-empirical equations⁷ have been proposed.

As yet there has been no satisfactory correlation of the surface potential measured by the method of Schulman and Rideal⁸ with the surface pressure and the known dipole moment of the molecule as measured *in vacuo*.⁹

The object of this paper is to consider a possible line of approach to this problem. The equation of state of an imperfect gas film is obtained, using the dissociation device and checked by the virial theorem; its application to real films is then discussed. In film theory, as in ordinary gas theory, the investigation of molecular interactions requires a knowledge of the temperature variation of the deviations from the perfect gas laws; unfortunately, the necessary data are not available for any substance sufficiently near the perfect gas region, so that at present comparison of theory and observation is not possible.

1. Perfect Gas Films.

The well-known results for a perfect two-dimensional gas can be obtained very simply, without assuming the validity of Maxwell's distribution law, by constructing the partition function for an assembly of N free molecules moving without interactions (apart from collisions) in a total accessible area A^X . At temperature T the partition function $H(T)$ for the actual assembly is obtained as the limit for quantised

¹ *Lieb. Ann.*, 1891, **155**, 27.

² *J. Amer. Chem. Soc.*, 1917, **39**, 1883.

³ *P.R.S.A.*, 1925, **109**, 57.

⁴ *P.R.S.A.*, 1926, **110**, 432.

⁵ See Topping, *P.R.S.A.*, 1928, **114**, 68.

⁶ *J. Franklin Inst.*, 1934, **218**, 143.

⁷ Volmer, *Z. physik. Chem.*, 1925, **115**, 255; Schofield and Rideal,³; Volmer and Mahnert, *Z. physik. Chem.*, 1925, **115**, 239; Bancroft, *J. Physic. Chem.*, 1927, **31**, 1501; Magnus, *Z. anorg. Chem.*, 1926, **150**, 311; and Tamamushi, *Bull. Soc. Chem. Japan*, 1927, **11**, 300.

⁸ *P.R.S.A.*, 1930, **130**, 259.

⁹ See Frumkin and Williams, *Proc. Nat. Acad. Sc., U.S.A.*, 1929, **15**, 400.

assemblies by making the extension of the element of phase space tend to zero; thus

$$H(T) = 2\pi mkT \frac{A^{\mathbf{x}}}{h^2} \quad . \quad . \quad . \quad (1)$$

and the surface pressure

$$\begin{aligned} F &= NkT \frac{\partial}{\partial A^{\mathbf{x}}} \log H(T) \\ &= \frac{NkT}{A^{\mathbf{x}}} \quad \text{or} \quad FA = kT \quad . \quad . \quad . \quad (2) \end{aligned}$$

where A is the area per molecule, so that if A is measured in \AA^2 , $k = 1.372$.

The observed total energy of the assembly

$$\bar{E} = NkT^2 \frac{\partial}{\partial T} \log H(T) = NkT \quad . \quad . \quad . \quad (3)$$

so that the molecules move in the film with mean kinetic energy kT .

The average number of molecules found in an element of area $dA^{\mathbf{x}}$ with velocity components lying between u and $u + du$, v and $v + dv$ is

$$\begin{aligned} \bar{a}, \quad \therefore \quad dndA^{\mathbf{x}} &= N \frac{\delta H(T)}{H(T)} \\ &= \frac{N}{2\pi mkT A^{\mathbf{x}}} e^{-\frac{m(u^2 + v^2)}{2kT}} m^2 du dv dx dy \\ \therefore \quad dn &= n \frac{m}{2\pi kT} e^{-\frac{m(u^2 + v^2)}{2kT}} du dv \quad . \quad . \quad . \quad (4) \end{aligned}$$

(where n is the molecular surface density) which is Maxwell's distribution law for the assembly.

2. The Equation of State of Imperfect Gas Films.

An imperfect gas film is discussed, using Boltzmann's device of regarding any pair of molecules within each other's field of force as a separate system and then obtaining the equilibrium properties by the dissociation theory of perfect gaseous assemblies.¹⁰ Thus, only binary interactions are considered. Most of the molecules investigated experimentally consist of a long hydrocarbon chain and a polar head group. In constructing a model, the flexible chain of the molecule is replaced by a rigid rotator with axial spin with its apex on the water surface and its centre of gravity at a distance $h^{\mathbf{x}}$ along the axis from the apex. The molecule is precessing about the normal to the water surface through the apex, and simultaneously undergoes its ordinary translational motion, making collisions with the other molecules. The polar head group is regarded as an electric dipole placed at the apex, and its orientation will be considered below. The details of the precessional motion and of the collision processes are not essential to the discussion, but it is the molecular interaction between the collisions that determines the deviation from the perfect gas laws. The force between two molecules is assumed to be radial, the potential energy of a molecular pair $E(r\theta_1\theta_2\phi_1\phi_2)$ being a function of the distance r between the mean positions of the centres of gravity, which are taken to lie on the normals through

¹⁰ See R. H. Fowler, *Statistical Mechanics*, Cambridge, 1929, p. 209.

the apices. Knowledge of the exact form of E is not necessary at present, and will be considered later.

The kinetic energy of rotation of each molecule is

$$T_{\text{rot}} = \frac{p_\theta^2}{2A} + \frac{(p_\phi - p_\psi \cos \theta)^2}{2A \sin^2 \theta} + \frac{p_\psi^2}{2C} \quad (5)$$

where θ, ϕ, ψ are the usual Eulerian angles and A and C are the transverse and axial moments of inertia; the corresponding potential energy due to the height of the molecular centre of gravity above the apex is

$$V = mgh^X \cos \theta$$

where m is the mass of the molecule.

An assembly of N similar molecules is considered. Let $f(T)$ be the partition function for the free systems, of number N_1 and average number \bar{N}_1 ; and similarly, let $g(T)$ be the partition function for the interacting pairs whose number is N_2 , and average number \bar{N}_2 . \bar{N}_2 is assumed to be small with respect to N and \bar{N}_1 .

Then

$$f(T) = \frac{m^2}{h^5} \iint_{A^X} \iint_{uv=-\infty}^{+\infty} \iiint_{p_\theta p_\phi p_\psi=-\infty}^{+\infty} \int_{\theta=0}^{\pi/2} \int_{\phi=\psi=0}^{2\pi} \exp. - \frac{1}{kT} \left\{ \frac{m}{2} (u^2 + v^2) + \frac{p_\theta^2}{2A} + \frac{(p_\phi - p_\psi \cos \theta)^2}{2A \sin^2 \theta} + \frac{p_\psi^2}{2C} + mgh^X \cos \theta \right\} dx dy du dv dp_\theta dp_\phi dp_\psi d\theta d\phi d\psi = (2\pi)^2 A C^{\frac{1}{2}} \frac{(2\pi kT)^{\frac{3}{2}}}{h^5} \frac{kT}{mgh^X} \left(1 - e^{-\frac{mgh^X}{T}} \right) 2\pi m kT A^X \quad (6)$$

Considering the interacting molecules, the weight to be attached to the element of phase space for the pair is

$$\frac{m^4}{\sigma h^{10}} du_1 dv_1 dx_1 dy_1 dp_{\theta_1} dp_{\phi_1} dp_{\psi_1} d\theta_1 d\phi_1 d\psi_1 du_2 dv_2 dx_2 dy_2 dp_{\theta_2} dp_{\phi_2} dp_{\psi_2} d\theta_2 d\phi_2 d\psi_2 \quad (7)$$

where the symmetry number $\sigma = 1$ if the molecules are not parallel, but $\sigma = 2$ if the molecules are parallel and the p_ψ 's are not different.

The corresponding energy is

$$\epsilon = \frac{1}{2} m(u_1^2 + v_1^2) + \frac{1}{2} m(u_2^2 + v_2^2) + T_{\text{rot.1}} + T_{\text{rot.2}} + mgh^X (\cos \theta_1 + \cos \theta_2) + E(r\theta_1\theta_2\phi_1\phi_2) \quad (8)$$

and by transforming to motion of the centre of gravity described by x, y, u, v and relative motion described by ζ, η, U, V the energy becomes

$$\epsilon = \frac{1}{2} (2m) (\Sigma u^2) + \frac{1}{2} \left(\frac{m}{2} \right) \Sigma U^2 + T_{\text{rot.1}} + T_{\text{rot.2}} + mgh^X (\cos \theta_1 + \cos \theta_2) + E(\sqrt{\zeta^2 + \eta^2} \theta_1 \theta_2 \phi_1 \phi_2) \quad (9)$$

The Jacobian of the transformation is unity, and hence after reduction the partition function becomes

$$g(T) = (2\pi)^2 A^2 C (2\pi kT)^3 \frac{A^X (2\pi m kT)^2}{\sigma h^{10}} \int_a \int_{\theta_1, \theta_2=0}^{\pi/2} \int_{\phi_1, \phi_2=0}^{2\pi} e^{-\frac{mgh^X}{kT} (\cos \theta_1 + \cos \theta_2) - \frac{E(\sqrt{\zeta^2 + \eta^2} \theta_1 \theta_2 \phi_1 \phi_2)}{kT}} d\zeta d\eta \sin \theta_1 d\theta_1 \sin \theta_2 d\theta_2 d\phi_1 d\phi_2 \quad (10)$$

where a is the area over which interaction is appreciable.

This is exact, but when E is independent of $\theta_1\theta_2\phi_1\phi_2$

$$g(T) = (2\pi)^4 A^2 C (2\pi kT)^3 A^X \frac{(2\pi m kT)^3}{h^{10}} \left(\frac{kT}{mg h^X} \right)^3 \left(1 - e^{-\frac{mg h^X}{kT}} \right)^2 B(T),$$

where
$$B(T) = \frac{1}{2} \int \int_a e^{-\frac{E(\sqrt{\eta^2 + \eta^2})}{kT}} d\zeta d\eta \quad (11)$$

By classical dissociation theory

$$\frac{N_2}{(\overline{N}_1)^2} = \frac{g(T)}{f(T)^2} = \frac{B(T)}{A^X} \quad \therefore \quad \overline{N}_1 = N - \frac{2B(T)N^2}{A^X}.$$

To obtain the equilibrium properties of the assembly, Planck's characteristic function ψ must be evaluated, and

$$\frac{\psi}{k} = \overline{N}_1 \left\{ \log \frac{f(T)}{\overline{N}_1} + 1 \right\} + \overline{N}_2 \left\{ \log \frac{g(T)}{\overline{N}_2} + 1 \right\} \quad (12)$$

The exact A^X factors in the partition functions are $A^X = \frac{Na}{2}$, so that

$$f(T) = \left(A^X - \frac{Na}{2} \right) F(T) \quad \text{and} \quad g(T) = \frac{B(T)}{A^X} \left(A^X - N \frac{a}{2} \right)^2 F(T)^2$$

$$\therefore \frac{\psi}{k} = N \left\{ \log \left(\frac{A^X F(T)}{N} \right) + 1 \right\} + \frac{N^2}{A^X} \left\{ B(T) - \frac{a}{2} \right\} \quad (13)$$

The surface pressure of the assembly is obtained immediately by differentiating,

$$F = T \frac{\partial \psi}{\partial A^X} = \frac{NkT}{A^X} - \frac{N^2 kT}{A^{X^2}} \left(B(T) - \frac{a}{2} \right) \quad (14)$$

$$\therefore FA = kT - \frac{\pi kT}{A} \int_0^\infty \left(e^{-\frac{E(r)}{kT}} - 1 \right) r dr \quad (15)$$

This result can be checked immediately by using the virial theorem in conjunction with Boltzmann's distribution law. In the usual notation

$$FA^X = \frac{1}{2} \sum m(\dot{x}^2 + \dot{y}^2) - \frac{1}{2} \sum r \frac{\partial E}{\partial r} \quad (16)$$

where the summation in the first term is over all the molecules, and in the second term over all molecular pairs. The average number of such pairs at a distance apart between r and $r + dr$ is

$$\frac{M^2}{2} \frac{2\pi r dr}{A^X} e^{-\frac{E(r)}{kT}} \quad (17)$$

and hence by simple reduction the equation of state is obtained

$$FA = kT - \frac{\pi kT}{A} \int_0^\infty \left(e^{-\frac{E(r)}{kT}} - 1 \right) r dr \quad (15)^*$$

3. The Molecular Model.

The application of this equation of state to real films demands a detailed knowledge of the form of $E(r\theta_1\theta_2\phi_1\phi_2)$. The exact relation of the water surface to the film molecule is uncertain, but the dipoles must be regarded as immersed in a medium of dielectric constant ϵ which

* The Laplace method of calculating the force across a line in the surface does not appear to give a unique result.

almost certainly is very much less than that of water in bulk. If the axes of the dipoles are fixed along those of the molecules, the dipole interactions contribute to E

$$\frac{\mu^2}{\epsilon r^3} \left\{ \cos \theta_1 \cos \theta_2 + \sin \theta_1 \sin \theta_2 \left[\cos (\phi_1 - \phi_2) \right. \right. \\ \left. \left. + 3 \frac{[\cos \theta_1 \sin \theta_2 - \cos \theta_2 \sin \theta_1 \cos (\phi_1 - \phi_2)][\cos \theta_2 \sin \theta_1 - \cos \theta_1 \sin \theta_2 \cos (\phi_1 - \phi_2)]}{\cos^2 \theta_1 \sin^2 \theta_2 + \cos^2 \theta_2 \sin^2 \theta_1 - 2 \cos \theta_1 \cos \theta_2 \sin \theta_1 \sin \theta_2 \cos (\phi_1 - \phi_2)} \right] \right\} \quad (18)$$

where μ is the dipole moment measured *in vacuo*.

Insertion of this expression in $g(T)$ gives an apparently intractable expression; however, a great simplification can be made by assuming that, over a wide range of areas, the dipole remains normally orientated with respect to the water surface. This model seems reasonable physically, and is in agreement with the known low value of the temperature coefficient of the surface potential. This assumption will be used in the rest of this paper, so that the dipole interactions are always repulsions, and contribute $\frac{\mu^2}{\epsilon r^3}$ to $E(r)$.

To account for the remaining and usually much more important part of the interaction energy, the device of classical gas theory of regarding the chains as impenetrable cylinders surrounded by weak attractive fields seems a suitable first approximation for films. The van der Waals' attractive field is probably most accurately represented by an inverse seventh power force,¹¹ so that the total interaction energy is of the form

$$E(r) = W(\sigma) + \frac{\mu^2}{\epsilon r^3} - \frac{\lambda}{r^6} \quad (19)$$

where $W = +\infty$ when $r < \sigma$ and $W = 0$ when $r > \sigma$.

σ probably corresponds to the measured cross-section of the chain. It is certainly possible to account for the compressibility of the molecules by representing the intrinsic field by an inverse power law or by an exponential function¹² instead of the admittedly crude impenetrable cylinder, but at the present stage of the theory such refinement is unnecessary. A simple numerical calculation shows that the effect of the gravitational field on the films is negligible.

Insertion of equation (19) in equation (15) leads immediately to the result

$$F - \frac{kT}{A} = \frac{kT\pi\sigma^2}{2A^2} - \frac{\pi kT}{A^2} \int_{\sigma}^{\infty} \left(e^{\frac{\lambda}{\epsilon kT r^6}} - \frac{\mu^2}{\epsilon kT r^3} - 1 \right) r dr \quad (20)$$

as a first approximation for the deviation from the perfect gas laws. A slight modification that is more suitable for attempted computation is

$$F - \frac{kT}{A} = \frac{kT\pi\sigma^2}{2A^2} - \frac{\pi kT}{3A^2} \left(\frac{\mu^2}{\epsilon kT} \right)^{\frac{1}{3}} \int_0^{\frac{\mu^2}{\epsilon kT \sigma^3}} \left(e^{\frac{\lambda \epsilon^{\frac{1}{3}} kT}{\mu^4} x^2 - x} - 1 \right) x^{-\frac{1}{3}} dx \quad (21)$$

4. Introduction of Surface Potentials.

The correlation of the dipole moments, as measured *in vacuo* with those measured by the surface potential method, is an extremely difficult problem. One very simple method of approach which may be suggested

¹¹ London, *Z. physik. Chem.*, 1930, **11**, 222.

¹² See Slater, *Physical Rev.*, 1931, **37**, 696.

depends on the fact that ΔV , n curve (n is the number of molecules /cm² of film) is often approximately linear over wide ranges of n , but for $n = 0$ the intercept on the ΔV axis ΔV_u , is not in general zero, being frequently negative for liquid expanded and vapour expanded films and positive for liquid condensed films. In this work it is assumed that the dipoles are orientated normally on the surface so that μ and $\bar{\mu}$, the vertical component, are identical.

The dielectric constant ϵ is obtained from the relation

$$\frac{\partial \Delta V}{\partial n} = \frac{4\pi\mu}{\epsilon} \quad (22)$$

using the observed value of $\frac{\partial \Delta V}{\partial n}$ and the vacuum value of μ . Then the effective moment μ_{eff} , which is to be used in equation (21) is obtained from ΔV by Helmholtz's equation

$$\mu_{\text{eff}} = \frac{\epsilon}{4\pi} A \Delta V \quad (23)$$

and equation (21) becomes

$$F = \frac{kT}{A} = \frac{kT\pi\sigma^2}{2A^2} - \frac{1}{3} \left(\frac{\epsilon}{16} \right)^{\frac{2}{3}} \left(\frac{kT}{\pi} \right)^{\frac{1}{3}} \frac{(\Delta V)^{\frac{1}{3}}}{A^{\frac{1}{3}}} \int_0^{\frac{\epsilon(A\Delta V)^{\frac{2}{3}}}{16\pi^2 kT\sigma^2}} \left(\frac{16\pi^2 kT}{\epsilon^2 (A\Delta V)^{\frac{2}{3}}} x^2 - x - 1 \right) x^{-\frac{1}{3}} dx \quad (24)$$

This method of obtaining the effective moment takes into account the underlying substrate, and is identical with that suggested by Schulman and Hughes¹³ since

$$\mu_{\text{eff}} = \mu_0 + \beta A \quad \text{where} \quad \mu_0 = \frac{\epsilon}{4\pi} A(\Delta V - \Delta V_u) \quad \text{and} \quad \beta = \frac{\epsilon}{4\pi} \Delta V_u \quad (25)$$

The interpretation suggested by these authors is that μ_0 is due to the film forming material itself, and is constant in any one state, while the term βA represents the manner in which the contribution due to the underlying solution varies with compression.

It is highly probable that the dielectric constant is really constant over a wide range of areas, and that electrostriction effects are negligible.

The further possibility remains that the re-orientation of the substrate molecules and the redistribution of the ions in the neighbourhood of the polar groups may introduce quadrupole interactions.

5. Comparison of Theory and Experiment.

Although numerous exact measurements of surface pressures and surface potentials have been made, a strict comparison of theory and experiment in terms of intermolecular forces is at present impossible, since the essential requirement for this is a knowledge of the temperature variations of the departures from the perfect gas laws; unfortunately, the necessary data are not available for any substances sufficiently near the perfect gas region. It is suggested that the most suitable method for presenting data obtained is to follow the Leiden method* that has

¹³ *P.R.S.A.*, 1932, **138**, 437.

* See Kamerlingh-Onnes, *Comm. Phys. Lab. Leiden*, No. 71, or *Proc. Sect. Sci., Amsterdam*, 1902, **4**, 125.

been used so successfully for ordinary gases, by expressing the surface pressure results in the form of an empirical equation of state of the type

$$FA = a + \frac{b}{A} + \frac{c}{A^2} + \frac{d}{A^3} +$$

where the virial coefficients are functions of temperature, and giving in addition the ΔV - A curves at the various temperatures.

A not very rigorous attempt has been made to analyse the accurate data given by Adam and Harding¹⁴ for the liquid expanded films of the C_{16} nitrile at $20.3^\circ C.$, with the aid of equation (24). Using the vacuum value of the dipole moment given by Smyth (*Dielectric Constants and Molecular Structure*, Appendix I.) and quoted by Adam and Harding, the value of ϵ obtained by equation (22) is constant over the liquid expanded region, and is approximately 15.8. This result is considerably higher than the values previously suggested because account has been taken of the non-zero value of ΔV_u , which here is + 89 mv. The order of magnitude of the attractive field constant has been determined, by adjusting, by means of variation of λ , coincidence of the observed Boyle point and that given by equation (24) when the terms of higher order are assumed to be zero. The integrals were evaluated by quadrature as expansion in series was not justifiable. The value of λ obtained was $62 \cdot 10^{-60}$, and is of the correct order, assuming additivity of the van der Waals fields.¹⁵ This method, of course, cannot give the correct variation of $F - \frac{kT}{A}$ with A at constant temperature.

Finally, I wish to express my thanks to Professor E. K. Rideal for his continuous interest and stimulating criticism, to Professor R. H. Fowler for a helpful discussion, and to many of the workers in this laboratory for valuable suggestions.

Summary.

The equation of state of an imperfect gas film is obtained and a method of correlating the surface potential with the deviation from the perfect gas laws is tentatively suggested. It is shown that exact comparison of theory and experiment is at present impossible, owing to lack of measurements giving the temperature variation both of the departures from the perfect gas laws and of the surface potentials. A method of collecting data analogous to the Leiden method for gases is suggested.

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Cambridge.*

¹⁵ See Lennard-Jones, *Proc. Lond. Physic Soc.*, 1931, **43**, 461.

¹⁴ *P.R.S.A.*, 1933, **143**, 104.

THE VELOCITY OF REACTION OF SODIUM ATOMS WITH CHLORO-, BROMO- AND IODO-BENZENE.

BY FRED FAIRBROTHER AND ERNEST WARHURST.

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Many measurements have been made of the rates of reaction of sodium atoms with inorganic halides and alkyl halogen compounds,¹ but few of the rates of reaction of sodium atoms with halogen-substituted benzene compounds. The published results in the latter direction appear to be confined to single estimations (which were stated to be only of an approximate nature) of the rates of reaction of sodium with chloro-benzene, bromo-benzene, iodo-benzene, benzoyl chloride, and benzyl chloride, carried out by Hartel and Polanyi² by the diffusion-flame method.

Special interest, however, attaches to the study in this connection, of aromatic halogen compounds, particularly in view of the importance of the general problem of aromatic substitution and of the possibility of obtaining information from such experiments, of the effect of different substituents in the benzene nucleus upon the strength of the carbon-halogen bond.

As a start in this direction we have measured the velocities of reaction of sodium atoms with chloro-, bromo- and iodo-benzene by the "life-period" method. This method, whilst much more laborious in its present form than the diffusion-flame method, is of wider applicability and, since less assumptions are involved, yields results which are more nearly "absolute." The principle of the method is as follows: one of the reacting partners (A) is led through a nozzle into the reaction vessel where it meets the other reactant (B) in such excess amount that the whole of the atoms of A react before they can reach the walls of the reaction vessel. If the concentration c of B is kept uniform over the reaction zone, then the amount of reaction occurring per second in a small element of volume dv is given by $kcc'dv$ where k is the velocity constant and c' is the concentration of the reactant A in the volume dv .

The total reaction in the vessel will therefore be given by $k c \int c' dv$ summed over the whole reaction zone. But $\int c' dv$ (expressed in appropriate units) is equal to the total number N of atoms of A present in the reaction chamber at a stationary state of the reaction: in addition, the total amount of reaction is equal to the total number of atoms n , of A, entering the reaction vessel per second, since we have assumed that the whole of A is consumed before it reaches the walls.

$$\text{Hence} \quad n = kcN \quad \text{or} \quad k = \frac{1}{c} \cdot \frac{n}{N}$$

¹ M. Polanyi, "Atomic Reactions" (Williams & Norgate), London, 1932; Schay, *Fortschritte Chem.*, 1930, 21.

² Hartel and Polanyi, *Z. physikal. Chem.*, 1930, 11B, 97.

and since $\frac{N}{n} = \tau$ is the average life of an atom of A in the reaction vessel,

$$k = \frac{1}{\tau} \cdot \frac{1}{c}.$$

It is required therefore, to know the rate of entry of atoms of A into the reaction vessel and the total number present at the stationary state and also the uniform concentration of B in the vessel.

Frommer and Polanyi³ have used this method to measure the rates of reaction between sodium atoms and volatile alkyl halogen compounds, the number, N , of sodium atoms in the reaction vessel at the stationary state being measured photographically by the absorption of sodium resonance light.*

In the present work, the experimental method was similar to that used by Frommer and Polanyi,³ with the inclusion of several modifications to increase the facility and accuracy of the measurements and to extend the scope of the method to less volatile halogen compounds.

Experimental.

The experimental arrangement is shown in Fig. 1: A stream of carrier gas, in the present case hydrogen, was circulated round the apparatus in the direction of the arrows, at a pressure of about 5 to 9 mm., picking up, in the process of circulation, sodium vapour from the molten sodium in the vessel S, and vapour of the halogen compound contained in the vessel H. In the method described by Frommer and Polanyi, the halogen compound was admitted to the reaction vessel through a capillary flowmeter, under the pressure of its own vapour. This could obviously not be done in the case of aromatic halogen compounds, owing to their much smaller vapour pressures, unless the whole apparatus were heated, which was clearly inconvenient. The circulating stream of hydrogen was therefore divided, as shown at Y in the diagram, into two approximately equal flows, which were made more definite by the inclusion of small resistances (K_1 , K_2) in the form of a short length (7 cm.) of 5 mm. diameter tubing, in each path.

The total speed of circulation of carrier gas was estimated by the pressure gradient across the capillary K_1 as measured by the double McLeod gauge. This capillary flowmeter was calibrated *in situ*, by passing a known volume of hydrogen (measured moist in a large gas-holder, and dried by a liquid air trap) at a constant speed through the apparatus. This calibration hydrogen entered the apparatus through a temporary connection at J and left through the tap 8. A series of rates of flow were employed and a "capillary constant" (K_1), in the expression

$$\text{Moles H}_2 \text{ passing per second} = \frac{K}{2} (P_1^2 - P_2^2) \quad . \quad . \quad (1)$$

(where P_1 and P_2 are the pressures at the ends of the capillary) obtained for the flowmeter. This method of calibration, almost under the conditions

³ Frommer and Polanyi, *Trans. Faraday Soc.*, 1934, **30**, 519.

* Cremer, Curry and Polanyi,¹ have also independently used this method to study the reactions of hydrogen atoms with a number of alkyl halogen compounds. The concentration of hydrogen atoms in the measured stream of hydrogen entering the reaction vessel and the number of hydrogen atoms present at the stationary state of the reaction, were measured by the rate of conversion of *para* hydrogen into the *ortho-para* equilibrium mixture.²

¹ Cremer, Curry and Polanyi, *Z. physikal. Chem.*, 1933, **23B**, 445.

² Farkas, *ibid*, *Chem*, 1930, **10B**, 419.

of the actual experiments, is preferable to calculation of the "capillary constant" from the dimensions of the capillary.

The evaluation of the relative magnitudes of the resistances K_2 and K_3 , and their associated tubes, and therefore of the relative amounts of carrier gas flowing along the two paths, was carried out as follows. Hydrogen at a pressure of about 6 mm. was circulated through the apparatus by means of the pump Z, all the taps except Nos. 2, 4, 5, 8 and 10 being open, and the total rate of flow measured by the pressure gradient across K_1 . The pressures at the two ends of the divided flow (the two circuits containing K_2 and K_3 acting as two resistances in parallel) were measured by the two single McLeod gauges M_1 and M_2 . These observations were continued over a period of about thirty minutes, and the mean values substituted in equation (1) to give the "capillary constant" K_4 of the capillaries K_2 and K_3 in parallel, together with any resistance between the single McLeod gauge M_1 and the point Y, and between the exit from the reaction vessel G and the single McLeod gauge M_2 .

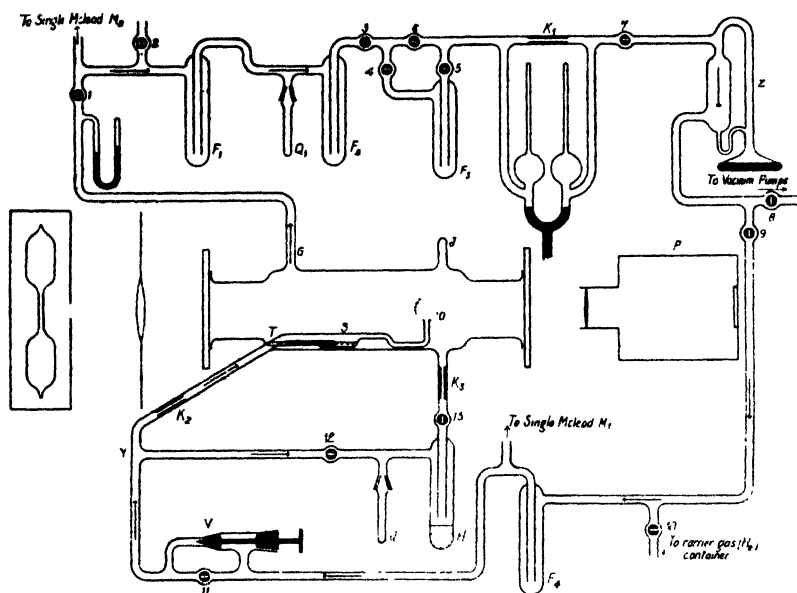


FIG. 1.

The experiment was then repeated with taps 12 and 13 closed, giving a corresponding value for the capillary K_2 and the rest of the circuit. The capillary K_2 was then removed and the interchangeable ground joints into which it fitted, closed by suitable stoppers. The experiment was then repeated with taps 12 and 13 open, giving a value for the "halide circuit." From these results the effect of the resistances between G and M_2 and between Y and M_1 could be eliminated by a simple calculation and the true resistances of the two circuits obtained. In this way it was found that for the sodium circuit, $K_2 = 5.71 \times 10^{-5}$ and for the halide circuit, $K_3 = 6.41 \times 10^{-5}$. Hence, the total flow of carrier gas divided at Y in the ratio of 5.71 (sodium) : 6.41 (halide). The adjustment of the total flow (which required to be carried out to within fine limits in order to obtain suitable operating conditions) was made by the Hauschild valve V.⁴

The second major modification of the method of Frommer and Polanyi

⁴ Hauschild, *Chem. Fabr.*, 1934, 7, 27.

was the use of a thin layer of directly excited sodium vapour as the illuminant in place of the very inconvenient indirectly excited sodium resonance light. The construction and operation of the electrodeless metal vapour lamp used for this purpose have already been described by J. L. Tuck and one of the present authors.⁵ Although the sodium vapour in this lamp is directly excited and therefore contains other radiation than the absorbable resonance radiation, the quality and relative intensity of the latter is such that the percentage of the total emitted radiation which is absorbed by a given mass of sodium vapour is actually greater than in the case of the indirectly excited radiation previously used. This has been attained by the use of a thin (≈ 2 mm.) layer of sodium vapour at a low pressure (10^{-5} mm.) excited by a high-frequency alternating current. In the present work the actual frequency used was 6.7×10^7 cycles per second, corresponding to a wave-length in air of 4.5 metres. This electrodeless vapour lamp is also much more convenient and constant in use and has reduced the necessary exposure (and therefore the time necessary to keep the flows, temperatures, etc. constant) from 10 minutes to 1 minute.

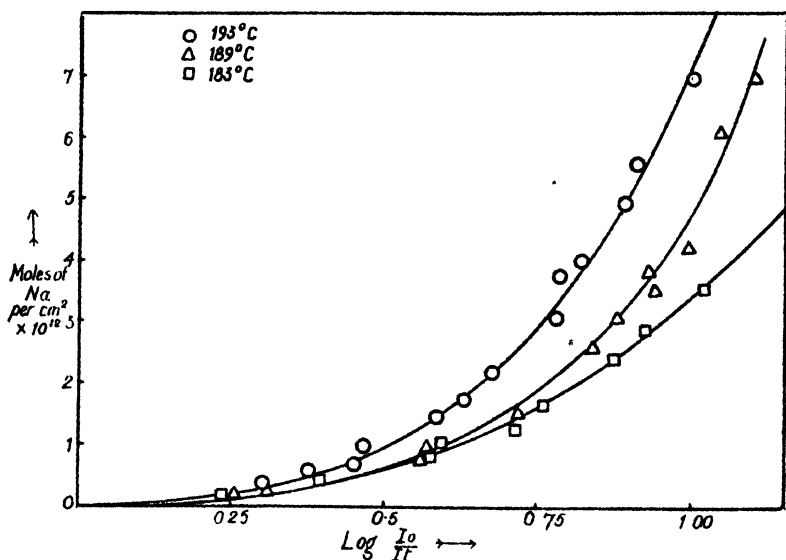


FIG. 2.

The lamp was housed in an electrically heated oven made of thick asbestos. Since the absorbability of the light is a function (*inter alia*) of the pressure of sodium vapour in the lamp, careful control of the temperature of the latter was necessary. This is illustrated by Fig. 2 in which the absorption, as $\log. (\text{Incident light } I_0) / \log. (\text{Transmitted light } I_t)$, is plotted as a function of the number of moles of sodium per square cm. in the path of the light: this has been done for three temperatures of the sodium lamp. The curves were obtained by the photographic method described below. The temperatures given in Fig. 2 were approximately the temperatures of the coldest part of the lamp tube. In practice, three thermometers were used, near the middle and two ends of the lamp tube respectively, and the temperature of the oven adjusted so that all three (which differed slightly among themselves) showed the same temperature in an actual reaction experiment (including the blank experiments) as in the measurements of the absorbability of the sodium light.

⁵ Fairbrother and Tuck, *Trans. Faraday Soc.*, 1935, **31**, 520.

Estimation of n .—The estimation of the number of sodium atoms entering the reaction chamber per second was made from the number of moles of hydrogen flowing through this part of the circuit and the relative partial pressures of the hydrogen and the liquid sodium in the boat S. The latter was obtained from the temperature of the sodium (as indicated by the thermometer T and which was also approximately that of the whole reaction vessel) and the vapour pressure data of Ladenburg and Thiele.* This method of calculation assumes that the carrier gas was saturated with sodium vapour at the saturation vapour pressure corresponding to the temperature of the sodium, an assumption which is probably very nearly correct in consequence of the large area of contact between the hydrogen and the liquid sodium and the low atomic weight of the latter. Previous workers with similar arrangements moreover, have found experimentally that this is the case.

Estimation of c .—A sufficient quantity of the purified halogen compound was placed in the tube Q_2 and freed from dissolved gases by several distillations *in vacuo* at room temperature. The apparatus was evacuated to a pressure of $\approx 10^{-4}$ mm. and the halide distilled in the closed apparatus between Q_2 and H_1 the receiver in each case being cooled in liquid air. The vessel H was of the form of an ordinary liquid air trap, with a slightly shortened centre tube: it was in this vessel that the halide vapour was picked up by the carrier gas. It is clear that the uniform concentration c , of halide in the reaction vessel, could be calculated from the flows of carrier gas through the capillaries and the partial pressure of the halide in the stream through K_3 , provided that this latter pressure were known. It could not be assumed however, that the carrier gas became saturated with the halide in its passage through H, as could be done with sufficient accuracy in the case of the sodium: in the first place the area of halide exposed was much less, and secondly the molecular weight of the saturating vapour was greater and the rate of diffusion from the liquid surface correspondingly less. The actual partial pressure of the halide was therefore estimated, under the actual conditions of the experiments, in the following manner. The vessel H containing the halide was immersed in a solution of solid carbon dioxide in acetone of a suitable temperature, contained in a Dewar vessel. (It was found that this simple arrangement gave a sufficiently constant temperature over the period required for the experiments.) The carrier gas was then circulated through the apparatus, the reaction vessel and sodium being at room temperature, and the volatilised halide condensed by liquid air, in the trap F_1 or F_2 from whence it was distilled into the tube Q_1 which was cooled in liquid air and afterwards removed, stoppered and weighed. Control experiments showed that a single trap was sufficient to condense all the halide. By carrying out a series of such experiments, in which the rates of flow of carrier gas and the temperature of the halide were approximately those of actual "reaction" experiments, the partial pressure of the halide in the gas stream through K_3 and therefore the quantity c , could be obtained by interpolation. As a result of these experiments it was found that the carrier gas took up the halide in its passage through H, at a pressure which was only about $\frac{1}{4}$ to $\frac{1}{3}$ of the saturation pressure of the halide at the temperature in question. Probably this wide discrepancy may have been due to the design of H. It was found that the actual partial pressure of the halide in the carrier gas stream, varied with the temperature of H, like a saturation vapour pressure, the plot of $\log. p$ against $1/T$ being a straight line: this greatly facilitated subsequent interpolation.

The estimation of N , the total number of sodium atoms in the reaction zone, was carried out photographically in much the same manner as described by Frommer and Polanyi, and involved the following operations:

* Ladenburg and Thiele, *Z. physikal. Chem.* 1930, **7B**, 161.

1. the calibration of a logarithmically darkened neutral wedge by means of a Zeiss "Stupho Photometer," whence the relation "Distance along wedge—log. (Incident light I_0 /Transmitted light I_T)," was obtained.
2. the making of a contact print of this wedge on a photographic plate, using the diffuse light from the sodium lamp.
3. a blank exposure of one minute duration, of a plate in the camera P, to the sodium light.
4. an exposure of one minute duration, of an actual reaction "flame" at O (which appears as a dark shadow owing to the absorption of the light by the sodium atoms.)
5. a repetition of the blank experiment 3.

The camera P was throughout focussed on to the nozzle O. The photographic plates were all of the same make and batch and were given identical treatment in development. Subsequent measurement of the plates was carried out by a visual photometer in which the various areas measured were compared with a movable neutral wedge of a logarithmic gradation in density. This photometer and its wedge acted essentially as an intermediary whereby areas on the blanks and reaction photographs respectively (defined by identical gratings of 2.5 mm. squares) were referred to positions of equal blackness on the contact photograph of the calibrated wedge (2). Since the opacity of this latter wedge could be expressed as

$$\text{Opacity} = \log. \frac{I_0}{I_T} = a + bl$$

where a and b are constants and l is the distance from some arbitrary zero,

$$\Delta \text{Opacity} = b\Delta l = -\Delta \log. I_T.$$

Hence the length between two positions of given blackness on the contact print of this wedge, could be expressed as $\Delta \log. I_T$. The photometer readings were therefore immediately transformed into terms of $\log. I_T$ where I_T is in each case the relative intensity of the light falling on the photographic plate over the small area in question: this was done by means of a curve representing the relation between the photometer readings and distances along the contact print (2) measured from an arbitrary zero. These values of $\log. I_T$ were then plotted against the distance from the centre of the nozzle for each 2.5 mm. strip of the photograph in the case of the blanks and reaction exposures. Smooth curves were drawn through these points and differences of the logs. of intensities in the two cases taken at equal distances from the nozzle centre. Since

$$\Delta \log. I_T = \log. \frac{I_T(\text{blank})}{I_T(\text{reaction})}$$

is a measure of the opacity of the sodium vapour in the particular region of the reaction zone which is being measured, these values could then be transformed into actual numbers of sodium atoms by means of the absorption measurements (*i.e.*, of $\Delta \log. I_T$ for a known mass of sodium vapour) shown in Fig. 2. Sodium distribution curves were then constructed for each strip of the sodium "flame" and the total number of sodium atoms in the reaction vessel computed by graphical integration.

The sodium absorption measurements given in Fig. 2 were made as follows: the sodium boat S was removed from the reaction vessel, and between the latter and the camera was interposed a cell C containing a known density of sodium vapour and a comparison prism P as shown in Fig. 3.* In this way the "blank" and the absorption photograph were obtained side by side on the same plate A. The lamp, reaction vessel and camera were mounted co-linearly on a 3 meter optical bench, the camera being

* We should like to thank Mr. J. L. Tuck for assistance with this part of the work.

movable, which facilitated this interposition. The sodium vapour was contained in a small Jena glass cell about 3 cm. diameter, with plane ends 4.64 cm. apart. Pure sodium was distilled *in vacuo* into this cell, which was then arranged in a capacious electrically heated air-oven. Condensation of sodium on the plane ends of the cell was prevented by the inclusion in the oven of small auxiliary heaters near the ends of the cell. The temperature was measured by three calibrated thermometers alongside the cell. The vapour pressure of the sodium and consequently the number of moles of sodium per unit area in the path of the light, were calculated from the

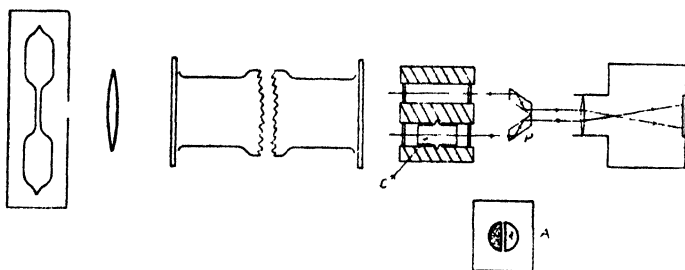


FIG. 3

observed temperature and the data of Ladenburg and Thiele⁶ extrapolated to the required region of temperature. The same photometer, calibrated wedge, and batch of photographic plates were used for these absorption measurements as for the "blank" and "reaction" photographs described above. $\log. \frac{I_0}{I_t}$ for the sodium cell corresponds to $\Delta \log. I_T$. The final results are given in Table I., in which the velocity constant k is expressed as moles per c.c. reacting per second, per unit molar concentration of each reactant per c.c.

Discussion.

It will be observed that there is an uncertainty in the final results for any one temperature of reaction, of nearly ± 20 per cent. This experimental error must be attributed to the accumulation of small errors in the numerous data from which the final results are obtained. In view of this margin of experimental error and the fact that the activation energies involved in the present reactions are all comparatively small, it will be immediately obvious that no reasonable estimate of the respective activation energies can be made from the temperature variation of the velocity constant over such ranges of temperature as used in these experiments. The present form of the reaction vessel sets a limit to the scope of the method in this direction, since the temperature of the sodium vessel is necessarily the same as that of the reaction zone. We hope to modify this feature of the apparatus in the near future.

An approximate value of the activation energy in each case, however, can be obtained from the collision yields in the reactions, assuming for the calculation of the number of collisions occurring per second, a probable "effective collision cross-section." Hartel and Polanyi² in their work on the reaction of sodium with a number of aliphatic halogen compounds by the diffusion-flame method, adopted 3.5×10^{-16} cm.² as a probable collision cross-section. They arrived at this

TABLE I.

Experiment No.	Date.	Halogen Compound.	Reaction Temperature. °C.	Total Reaction Vessel. mm. Hg.	Total Amount of H ₂ Circulating. Moles/sec.	Halogen Compound.				Sodium.						Velocity Constant, $\frac{1}{\tau \cdot c}$ Cm. ³ Mol./sec.	Velocity Constant, Mean Value of k . Cm. ³ Mol./sec.
						Amount of H ₂ Circulating through Halide Bath. Moles/sec.	Amount Entering Reaction Vessel. Moles/sec.	Pressure in Reaction Vessel. mm. Hg.	Concentration in Reaction Vessel C. Moles/cm. ³	Amount of H ₂ Circulating through Sodium Boat. Moles/sec.	Vapour Pressure at Reaction Temperature. mm. Hg.	Amount Entering Per Second in Moles n .	Stationary Quantity in Reaction Zone N. Moles.	Average Life Period of Sodium Atoms $\tau = \frac{N}{n}$. Seconds.			
08	22/11/34	PhCl	281.0	9.65	3.81×10^{-3}	1.08×10^{-3}	1.125	3.26×10^{-8}	4.36×10^{-3}	6.93×10^{-3}	3.13×10^{-8}	3.30×10^{-12}	1.05×10^{-4}	2.91×10^{11}	2.65×10^{11}		
09	"	"	281.0	8.80	3.30×10^{-3}	1.02×10^{-3}	1.10	3.21×10^{-8}	3.86×10^{-3}	6.93×10^{-3}	3.04×10^{-8}	3.97×10^{-12}	1.30×10^{-4}	2.38×10^{11}			
21	22/1/35	PhBr	244.0	7.75	1.01×10^{-3}	9.25×10^{-7}	3.72×10^{-2}	1.15×10^{-9}	9.1×10^{-3}	1.31×10^{-3}	1.54×10^{-8}	0.98×10^{-12}	6.35×10^{-4}	1.37×10^{12}	1.62×10^{12}		
23	"	"	242.9	7.55	9.68×10^{-5}	4.41×10^{-7}	1.81×10^{-2}	5.62×10^{-10}	8.62×10^{-3}	1.23×10^{-3}	1.43×10^{-8}	1.26×10^{-12}	8.81×10^{-4}	2.01×10^{12}			
33	8/2/35	"	244.8	6.4	1.05×10^{-4}	6.62×10^{-7}	2.13×10^{-2}	6.6×10^{-10}	9.3×10^{-3}	1.36×10^{-3}	1.98×10^{-8}	2.04×10^{-12}	1.03×10^{-4}	1.48×10^{12}	1.48×10^{12}		
34	"	"	222.6	6.1	1.26×10^{-4}	4.52×10^{-7}	1.16×10^{-2}	3.73×10^{-10}	1.12×10^{-4}	4.49×10^{-4}	8.24×10^{-9}	1.67×10^{-12}	2.03×10^{-4}	1.32×10^{12}			
35	"	"	223.1	5.9	1.18×10^{-4}	3.69×10^{-7}	9.78×10^{-3}	3.16×10^{-10}	1.04×10^{-4}	4.60×10^{-4}	8.15×10^{-9}	1.57×10^{-12}	1.93×10^{-4}	1.64×10^{12}	2.06×10^{12}		
39	1/3/35	PhI	225.2	7.6	1.24×10^{-4}	7.00×10^{-5}	2.26×10^{-3}	7.28×10^{-11}	1.11×10^{-4}	5.15×10^{-4}	7.52×10^{-9}	0.59×10^{-12}	7.85×10^{-5}	1.75×10^{12}			
40	"	"	225.2	7.45	1.11×10^{-4}	6.66×10^{-8}	2.36×10^{-3}	7.59×10^{-11}	0.99×10^{-4}	5.15×10^{-4}	6.84×10^{-9}	0.36×10^{-12}	5.26×10^{-5}	2.50×10^{12}	1.93×10^{12}		
41	"	"	230.6	7.2	1.21×10^{-4}	7.38×10^{-8}	2.31×10^{-3}	7.40×10^{-11}	1.09×10^{-4}	6.79×10^{-4}	1.03×10^{-8}	0.72×10^{-12}	7.00×10^{-5}	1.93×10^{12}			

average figure from a consideration of the collision cross-sections of such compounds, as obtained from gas viscosity measurements, with the realisation that the effective cross-section was not necessarily the same in the case of a reaction. Nevertheless, the assumption of such a collision cross-section enables approximate calculations to be made of the activation energies of the reactions and useful comparisons to be drawn which will not be qualitatively invalidated by any error likely to be made in the figure assumed for this cross-section. It should be emphasised, however, that this assumption is of an arbitrary nature.

Taking then the mean velocity constants in Table II., and the effective collision cross-section, which is equal to σ^2 , the square of the "collision diameter" in the

usual expression for the calculation of the total number of collisions Z , per second per unit volume,

$$Z_0 = \sigma^2 n_1 n_2 \sqrt{8\pi RT} \cdot \frac{M_1 + M_2}{M_1 M_2}$$

as 3.5×10^{-15} cm.², and calculating the activation energy A from the ⁷ equation $Z_e/Z_0 = e^{-A/RT}$ where Z_e/Z_0 is the collision yield, we obtain:—

The velocity constant in the case of the iodobenzene reaction may be subject to a slight inaccuracy on account of the fact that the

TABLE II.

Reaction.	t° .	Collision Yield.	Activation Energy.
$C_6H_5Cl + Na$	281°	1.1980	8,250 cals.
$C_6H_5Br + Na$	244°	1.303	3,520 cals.
$C_6H_5I + Na$	227°	1.231	835 cals

concentration of halide vapour at the mouth of the nozzle was not greatly in excess of the sodium concentration, as assumed in the theory. In the experiments given in Table II, the concentration of iodobenzene was about 4 times the concentration of sodium atoms in the "flame," whereas the relative concentrations of chloro- and bromo-benzene to sodium atoms were of the order of 160 and 20 respectively. This condition of affairs is inevitable with the present method, in the case of reactions occurring at nearly every collision, for an increase in the ratio of halide to sodium concentration results in the disappearance of the sodium "flame" except over a very small region above the nozzle exit. It may well be that the reaction between iodobenzene and sodium occurs at every, or nearly every, collision, with an activation energy which is too small to be measured.

Using the above activation energies, we may calculate for comparison the velocity constants at 244°, the temperature of the sodium-bromobenzene reaction, giving a ratio of velocities of

$$-Cl : -Br : -I \\ = 1365 : 13 : 1.$$

These velocity constants differ appreciably from those of Hartel and Polanyi,² which however,

as mentioned earlier, were stated by the authors to be approximate only.

The present results show a striking similarity to those obtained by previous workers with aliphatic halogen compounds, using the diffusion-flame method. For example, the velocity constants obtained by Hartel and Polanyi² for the methyl halides, when multiplied by a factor of $(8.3 \times 10^7 \times T)^2$ in order to transform them into the same units as used in the present paper give

⁷ Trautz, *Z. Elektrochem.*, 1909, **15**, 692.

Reaction.	T° .	$k(\text{cm.}^3 \text{mol.}^{-1} \text{sec.}^{-1})$.	Collision Yield.	Activation Energy.
$\text{CH}_3\text{Cl} + \text{Na}$	240°	7.8×10^{10}	1 : 5000	8,800 cal.
$\text{CH}_3\text{Br} + \text{Na}$	240°	2.35×10^{13}	1 : 25	3,200 cal.
$\text{CH}_3\text{I} + \text{Na}$	240°	3.35×10^{14}	1 : < 2	—

(The value for CH_3Cl has been calculated from the experimental data at 260° and the activation energy given.)

The ratio of velocities — Br : — I = 1 : 14 is nearly the same as the present results with the corresponding benzene halides, though the speed of the methyl chloride is relatively much less.

A comparison of the present results with some later unpublished results of Dr. Heller, also carried out by the diffusion-flame method, shows that the reactions between sodium and chlorobenzene and between sodium and bromobenzene are in each case about twice as fast as the corresponding reactions with the methyl halides. A similar ratio of two to one holds in the case of chlorobenzene and the earlier result of Polanyi and Hartel for methyl chloride, though these authors obtained velocity constants as shown above, for methyl bromide and iodide which are slightly greater than our results for bromo- and iodo-benzene, the *ratio* of the speeds being nearly the same in each case.

A comparison of the mean velocity constant of the reaction between chlorobenzene and sodium, with the values obtained by Hartel, Meer and Polanyi⁸ for a number of alkyl chlorides, shows that the velocity constant for the former reaction lies near to that for tertiary butyl chloride.

It may be concluded therefore that the present results show that the benzene halides react with sodium in the vapour phase as fast, or faster, than the corresponding simple aliphatic halides, and that the ratios of the speeds of the reactions — Cl : — Br : — I, is much the same in both series.

This result is very striking when compared with the well-known difference in resistance to solvent hydrolysis or negative ion attack of the two series of compounds, and emphasises the difference in actual mechanism in the different types of reaction.

We wish to defer a more detailed discussion of these mechanisms, but it may be pointed out that the essential difference as discussed by Meer and Polanyi⁹ between the reaction of a halogen compound with a sodium atom and with a negative ion respectively, is as follows :

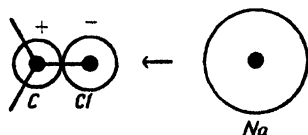


FIG. 4.

The sodium atom can approach the carbon-halogen dipole freely from the negative end, the final collision which results in reaction probably occurring in all cases as a "head-on" collision in the direction of the carbon-halogen bond. Such collisions can take place equally well when the halogen is at-

tached to a benzene nucleus as when it is attached to an aliphatic carbon atom.

The negative ion however, is repelled by the halogen atom, as this constitutes the negative end of the dipole. In the case of saturated

⁸ Hartel, Meer and Polanyi, *Z. physikal. Chem.* 1932, **19B**, 150.

⁹ Meer and Polanyi, *Z. physikal. Chem.*, 1932, **19B**, 164.

aliphatic halides, the ion is able to approach the carbon atom from a position well removed from the negative end of the dipole, by an attack at the rear of the carbon atom. In this it is assisted by the field of the dipole, and the reaction may lead to inversion of symmetry which, in the case of an optically active substance is shown by a change in the optical rotation.

In the case of nuclear aromatic halides, such an attack of the negative ion, from the rear of the carbon atom is not possible, for steric reasons, and the negative ion must approach the carbon atom from the side, necessarily relatively close to the negative end of the dipole, receiving little or no assistance from the field of the latter.

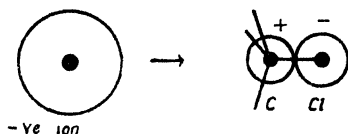


FIG. 5.

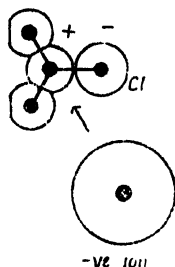


FIG. 6.

Moreover, since the ion can only form a bond in the direction of its approach, it is probable that a reaction necessitates a bending away of the carbon-halogen bond and the formation of a carbon-X bond (where X^- is the ion), which at the instant of its formation, is also not co-linear with the axis of the benzene ring. Both these latter effects will further increase the activation energy of the reaction of a nuclear aromatic halide with a negative ion.

Nevertheless, the smallness of the difference in activation energy required for a sodium atom to react with a chlorine atom when attached to a methyl group and a benzene nucleus is remarkable, for it has been shown by X-ray and electron diffraction experiments, that the length of the carbon-halogen bond is appreciably less in the case of aromatic halides than in aliphatic halides. De Laszlo,¹⁰ for example, gives the distances as

	Saturated Aliphatic.	Aromatic.
Carbon—chlorine	1.76 Å.	1.69 Å.
Carbon—bromine	1.93 Å.	1.88 Å.
Carbon—iodine	2.12 Å.	2.05 Å.

We must attribute this result to the great compressibility of the electronic systems of the carbon atoms in the benzene nucleus, for the present results

do not indicate that the halogen atom is bound more tightly to an aromatic carbon atom than to an aliphatic one.

Summary.

(1) The rates of reaction of chloro-, bromo-, and iodo-benzene with sodium vapour have been measured by the "life-period" method.

(2) The rates of reaction are of the same order as in the aliphatic series, being somewhat faster than the rates of reaction of sodium with the corresponding methyl compounds.

(3) The effect of the change of halogen atom on the relative rates of reaction, is much the same in the benzene halides as in the case of the corresponding aliphatic compounds.

¹⁰ de Laszlo, *Nature*, 1935, 135, 474.

(4) The similarity in reactivity of corresponding aliphatic and aromatic compounds in this respect, is briefly discussed.

In conclusion, we wish to thank Professor M. Polanyi for his help and advice throughout this work.

We also wish to thank Messrs. Imperial Chemical Industries Ltd., for a grant for the purchase of apparatus and the Department of Scientific and Industrial Research for a maintenance grant to one of us (E. W.)

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A MODIFICATION OF CARPENTER AND ELAM'S METHOD OF PRODUCING SINGLE CRYSTALS OF ALUMINIUM BY DEFORMATION AND ANNEALING.

BY VAUGHAN H. STOTT, M.Sc.

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Carpenter and Elam¹ prepared single crystals of aluminium from tensile test-pieces machined from hard rolled cylindrical bars. The specimens were first annealed for six hours at about 550° C. (The exact temperature differed somewhat with different batches of metal, and the best value was carefully determined by trials.) They were then stretched 2 per cent., or a little less, and again heated from 450° C. to 550° C. at the rate of 10° C. rise of temperature per day, held at 550° C. for two days, brought to 600° C., and held at that temperature for six hours.

Although not mentioned by Carpenter and Elam, the precise method of rolling the metal would appear to be of great importance. The present writer's experiments were begun on rolled bars remaining from a batch which had been successfully used by a colleague some five years earlier. It was found that a temperature of 575° C. had to be used for the first annealing, although in the earlier work a temperature of 550° C. was satisfactory. This difference in behaviour may be due to slight annealing of the metal at room temperatures during the interval of five years, but other explanations are possible.

Using new batches of metal, the writer was for a long time unable to obtain single crystals. Nevertheless, the best specimens always contained crystals extending the whole length of the narrower section of the test-piece. It was reasonable to suppose that these results were due to a lack of uniformity in the structure of the metal after rolling; for since round bars are reduced by successive passages through slightly curved V-shaped grooves, a cross section of the bar may contain a number of sectors which have been differently worked, the cross sections at different points along the length of the bar being similar to one another. The effects of such differences may be observed by etching the bar, which may then exhibit faint longitudinal stripes somewhat like those of a freshly mown lawn. In such cases a trace of the structure may be observed after the first annealing

¹ *Proc. Roy. Soc.*, 1921, **100A**, 345.

for six hours at a temperature of about 550°C ., the specimen for this purpose being etched for the first time after the annealing. It is not surprising that specimens having the appearance described yield several very long crystals on subsequent treatment. To obtain a single crystal, a method must be found for eliminating the slight differences between the various sectors. This may be done by stretching the specimen 10 per cent. and repeating the first annealing. For the metal used by the writer (0.08 per cent. silicon, 0.09 per cent. iron), and a temperature of 560°C . for both annealings, the linear dimensions of the grains in the treated metal are some fifteen times as great as was recommended by Carpenter. In spite of this, an extension of 1.7 per cent. followed by an annealing from 450°C . to 600°C . in the usual way, will produce a single crystal containing a few grains here and there which have not been absorbed. These grains may usually be removed by continuing the annealing to a temperature of 645°C . and maintaining this temperature for a few days.

The above procedure has been modified a little in later experiments. It is advantageous to increase the first extension of 10 per cent. to 15 per cent. The smaller grains then formed on annealing, are more readily absorbed in the next process. Larger extensions than 15 per cent. have not been tried. The material would probably elongate too unevenly, and in any case a great reduction in the diameter of the specimen is not wanted. For the last annealing, the present practice is to raise the temperature at the rate of 10°C . per day from 450°C . to 640°C ., and then maintain a temperature of 640°C . to 645°C . for a few days. The specimens are heated in a vertical position to prevent deformation under the action of gravity. Six specimens are usually annealed together, and not less than four crystals are obtained of length 7-inches, and diameter $\frac{1}{2}$ -inch. When a single crystal is not obtained the specimen consists of two large crystals. A yield of six single crystals has been obtained. These yields are considerably higher than those of Carpenter and Elam for specimens of comparable form and shape, and were obtained after unsuccessful attempts by their method.

The reason for the success of the modified method has been suggested above. It is not difficult to postulate the conditions which must be fulfilled to ensure the success of the Carpenter method. It has long been known that the internal energy of cold-worked aluminium is greater at a given temperature than that of the annealed metal. But G. I. Taylor¹ has shown that the increase of internal energy due to a given method, of deformation, is limited in amount, any work done on the metal above a certain value being dissipated in the form of heat. Very severe rolling may therefore be expected to yield a practically uniform structure across the section, provided that rupture of the metal is avoided. It is difficult in practice to adjust the conditions of rolling so as to obtain this uniform structure, and in all probability the bars used by the present writer had not been worked sufficiently. The modified process, although longer, is more reliable than the original process, and it is quite possible that the new process can be considerably shortened. It has been found that carrying out the first two annealings in five, instead of six hours each, makes no difference to the final result. The extension of 1.7 per cent. before the last annealing is probably very close to the optimum value. Single crystals are obtainable when the extension is between 1 and 2 per cent. An extension of $\frac{1}{2}$ per cent. is insufficient to produce any grain growth. An extension of 3 per cent. is too much for a single crystal, although one of the large crystals formed may extend the full length of the specimen.

For certain experiments, the Engineering Department of the Laboratory required single crystals containing a transverse cylindrical hole of $1/16$ inch diameter. To obtain such a specimen, a crystal was carefully bored with a very sharp drill, and annealed at temperatures rising slowly to 614°C . Etching showed that this specimen was satisfactory. If small holes are

¹ *Proc. Roy. Soc.*, 1934, **143A**, 307.

placed in a specimen either just before, or just after the 15 per cent. extension during the ordinary process of forming a single crystal, two crystals tend to be formed with a longitudinal irregular boundary passing through a longitudinal diameter of the hole.

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ON THE APPROXIMATE ESTIMATION OF THE CRITICAL CONSTANTS OF UNASSOCIATED SUBSTANCES.

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Received 19th June, 1935.

Despite the immense accumulation of experimental data, there are many gaps in the tables which record such commonplaces as density, viscosity, surface tension and the like. In particular it is specially difficult to find trustworthy values of critical data which cover a really wide range, and the simple calculations developed below are intended to assist the researcher who desires a first approximation to the critical data for an unassociated substance.

It has long been known that a useful approximation to the critical temperature for an unassociated liquid may be obtained from the assumption that the normal boiling-point on the Kelvin scale is two-thirds of the critical temperature.¹ The ratio is affected by constitution,² and the rule is, of course, no more than a convenient first approximation.

Recently, a long-range formula has been developed by one of us which represents with very considerable accuracy the relation between orthobaric density and temperature for an unassociated liquid over the whole range of its existence—from freezing-point to critical-point.^{3, 4} This relation may be written

$$\rho = 2\rho_c[A(1-m)^s + (1-0.5m)] \quad (1)$$

where ρ is the orthobaric density of the liquid at a reduced temperature m . A and s vary but slightly from liquid to liquid and, to a first approximation, we may put $A = 1$, $s = 0.3$.

This equation is deduced from the power law

$$\gamma = \gamma_0(1-m)^n \quad (2)$$

connecting surface tension and temperature, Macleod's equation

$$\gamma = C(\rho_l - \rho_v)^p \quad (3)$$

and the law of rectilinear diameters.

If we assume that $n = 1.2$, $p = 4$ and that the (absolute) zero density of the supercooled liquid is four times the critical density, we easily arrive at equation (1) with A equal to unity and s equal to 0.3.

¹ Guldberg, *Z. physik. Chem.*, 1890, 5, 374.

² Young, *Stoichiometry*, 1908, p. 183.

³ *Proc. Physic. Soc.*, 1932, 44, 121.

⁴ Ferguson and Miller, *Proc. Physic. Soc.*, 1934, 46, 140.

If the highest accuracy is desired, account must be taken of the slight variations of A and of s from substance to substance, but a graphical correction shows that very fair agreement with observation is obtained if we take A as 0.91 and s as 0.3. Our working equation for unassociated liquids is, therefore,

$$\rho = 2\rho_c[0.91(1 - m)^{0.3} + (1 - 0.5m)] \quad (4)$$

It is obviously a reduced equation of state, giving the relation between reduced orthobaric density and reduced temperature, and, in this form, cannot be expected to withstand more strain than do the majority of such equations. Nevertheless, certain deductions may be made from it which are in close agreement with experimental results. We may note, in passing, that if we put $m = 0$, we obtain for the zero density of the supercooled liquid,

$$\rho = 2\rho_c[0.91 + 1] = 3.82\rho_c \quad (5)$$

probably a better approximation than the usual value $4\rho_c$.

Equation (4) enables us to calculate the critical density, given a value of the orthobaric density at *any* one known reduced temperature m . The paper just quoted ⁴ gives a table of values of critical densities calculated from the densities of twenty-seven organic liquids taken at the reduced temperature $m = 0.6$. The agreement between the observed and calculated values is quite satisfactory. This method, which assumes a knowledge of the critical temperature, is the preferable way of estimating the critical density. If the critical temperature is not known we may make use of Guldberg's rule that the boiling-point is approximately two-thirds of the critical temperature. Putting, therefore, $m = \frac{2}{3}$ in equation (4) we have, for the density at the normal boiling-point

$$\rho_b = 2\rho_c[0.91(1 - \frac{2}{3})^{0.3} + (1 - 0.5 \times \frac{2}{3})],$$

or

$$\rho_b = 2.642\rho_c \quad (6)$$

a general relation between the density at the normal boiling-point and the critical density

The experiments of Young ⁵ have shewn that the value of $RT_c/p_c v_c$ is very fairly constant for unassociated substances, and its mean value may be taken as 3.83.

If we reckon pressures in atmospheres, we have

$$R \cdot \frac{T_c}{p_c v_c} = MR \cdot \frac{T_c}{p_c M v_c} = \frac{p_0 M v_0}{T_0} \cdot \frac{T_c}{M v_c \cdot p_c} = \frac{22,400}{273} \frac{T_c}{M v_c p_c} = \frac{82}{M} \frac{\rho_c T_c}{p_c},$$

v_c being the *specific* critical volume.

Putting, then,

$$\frac{82}{M} \cdot \frac{\rho_c T_c}{p_c} = 3.83 \quad (7)$$

and combining this with the boiling-point relations

$$T_b = \frac{2}{3}T_c, \text{ and } \rho_b = 2.642\rho_c,$$

we find that

$$\rho_b T_b = 0.0823 M p_c \quad (8)$$

a convenient equation from which to calculate the critical pressure.

⁵ Young, *Scientific Proc. Roy. Dublin Soc.*, 1910, 12, 374.

A more accurate method for arriving at an approximation to the critical temperature is based on the power law connecting surface tension and temperature. If we write this equation as

$$\gamma = \gamma_0(1 - cT)^n$$

we see that c is accurately the reciprocal of the critical temperature. Suppose, then, that we have a number of values of the surface tension of an unassociated liquid measured at different known temperatures between the freezing-point and the normal boiling-point. Various simple methods are known by which the constants in the power-law equation may be evaluated. One easy method is to work out a number of values of $d\gamma/dT$ at different temperatures and to plot the values of $\gamma \cdot dT/d\gamma$ against temperature. The plot is linear and the slope and intercept of the line so determined give the values of n and c .

If the critical temperature is thus determined, or is known experimentally, the following procedure may be employed to evaluate the critical density and pressure. If we put $m = 0.6$, which, for most substances, corresponds to a temperature conveniently below the normal boiling-point, we have, putting this value in equation (4),

$$p_c = 0.3592\rho \quad \dots \quad (9)$$

where ρ stands for the density of the liquid at the known reduced temperature 0.6.

Substituting these values in (7) we obtain

$$\rho T = 0.07804Mp_c \quad \dots \quad (10)$$

as an equation for p_c , ρ being the density at a temperature T which is six-tenths of the absolute critical temperature.

This, of course, amounts to no more than saying that, if one knows the critical temperature, and has some convenient method of calculating the critical density, the critical pressure may then be estimated from a knowledge of the mean value of the ratio $(RT_c)/(p_c v_c)$. This process is, in effect, followed by D. Berthelot,⁶ who estimates molecular weights by means of the equation

$$M = 11.4\rho \times \frac{T_c}{p_c \left(2 - \frac{T}{T_c}\right)}$$

The method is obscured a little, but the author (assuming the critical temperature and pressure to be known), calculates the critical density by a direct application of the law of rectilinear diameters, and then determines M by substituting the critical values in the equivalent of equation (7). He, however, assumes that the constant of this equation is 3.6, and that the zero density of the supercooled liquid is four times the critical density. The method, indeed, in this form, introduces unnecessary inaccuracy. For most substances for which we may assume an *experimental* value of p_c , the values of ρ_c and of T_c are also known experimentally, and it is, therefore, only necessary to substitute these values in equation (7) in order to arrive at a value for M .

Without unduly complicating matters, the calculations based on equation (7) may be considerably improved. Inspection of Young's results shows that the esters may be regarded as a separate class, in which the mean value of $RT_c/p_c v_c$ is 3.91; for the other unassociated substances

⁶ Young, *Stoichiometry*, 1908, p. 351.

examined by Young the values are distinctly lower and the average may be taken as 3.78. In the Tables which follow, Table I. refers to the esters

TABLE I.—ESTERS.

Substance.	$RT_0/p_0 v_0$	$T^\circ\text{C.}$	ρ_T	ρ_0 Obs.	ρ_0 Calc.	p_0 Obs.	p_0 Calc.
Methyl formate .	3.922	19.2	0.976	0.349	0.350	59.2	59.67
Methyl acetate .	3.943	33.4	0.916	0.325	0.329	46.3	47.62
Methyl propionate .	3.909	45.2	0.885	0.312	0.318	39.5	40.19
Methyl butyrate .	3.903	59.5	0.854	0.300	0.307	34.2	34.95
Methyl isobutyrate .	3.866	51.3	0.853	0.301	0.306	33.87	34.01
Ethyl formate .	3.895	31.9	0.907	0.323	0.326	46.76	46.89
Ethyl acetate .	3.949	40.8	0.875	0.308	0.314	38.00	39.13
Ethyl propionate .	3.923	53.5	0.852	0.296	0.306	33.18	34.21
Propyl formate .	3.869	49.6	0.870	0.309	0.313	40.08	40.01
Propyl acetate .	3.934	56.5	0.848	0.296	0.304	33.20	34.40

and Table II. to the other unassociated substances for which calculations

TABLE II.

Substance.	$RT_0/p_0 v_0$	$T^\circ\text{C.}$	ρ_T	ρ_0 Obs.	ρ_0 Calc.	p_0 Obs.	p_0 Calc.
Benzene .	3.755	63.7	0.832	0.304	0.298	45.70	46.63
Iodobenzene .	3.780	159.6	1.620	0.581	0.581	44.62	44.62
Bromobenzene .	3.809	129.0	1.345	0.485	0.483	44.62	44.72
Chlorobenzene .	3.776	106.3	1.012	0.365	0.364	44.60	44.31
Fluorobenzene .	3.796	62.7	0.971	0.354	0.349	44.60	44.09
Pentane .	3.766	9.1	0.637	0.232	0.229	33.03	32.37
Isopentane .	3.735	3.4	0.626	0.234	0.224	32.92	31.18
Hexane .	3.831	31.6	0.649	0.232	0.233	29.62	29.82
Heptane .	3.854	50.1	0.657	0.234	0.236	26.88	27.55
Octane .	3.865	68.5	0.662	0.233	0.238	24.64	25.74
Cyclohexane .	3.706	58.8	0.741	0.273	0.266	39.82	37.96
Di-isobutyl .	3.810	56.8	0.662	0.236	0.237	24.55	24.88
Di-isopropyl .	3.741	27.1	0.655	0.241	0.235	30.74	29.68
Ethyl ether .	3.813	7.0	0.728	0.262	0.262	35.28	35.75
Carbonyl chloride	3.680	60.6	1.515	0.558	0.544	44.98	42.67
Stannic chloride .	3.740	82.0	2.060	0.742	0.742	37.0	36.57

have been made. The equations from which the critical pressures have been calculated are,

$$\text{for esters, } \rho T = 0.07968 M p_0 \quad . \quad . \quad (11)$$

$$\text{for other substances, } \rho T = 0.07702 M p_0 \quad . \quad . \quad (12)$$

In the Tables the second column gives the values of $RT_0/p_0 v_0$ found by Young, the mean values of which have been used in computing equations (11) and (12). The third column indicates the temperatures (in degrees Centigrade) which are six-tenths of the absolute critical temperatures. The fourth column shows the densities at these temperatures, the densities being given in grams per cubic centimetre. In the fifth and sixth columns the observed and calculated values of the critical densities are compared, and in the seventh and eighth columns those of the critical pressures measured in atmospheres.

MAGNETIC PROPERTIES OF SOLUTIONS OF CADMIUM IN MOLTEN CADMIUM-CHLORIDE AND OF MOLTEN CALOMEL.

BY J. FARQUHARSON AND E. HEYMANN.

Received 13th May, 1935.

It has been known for a long time that several metals are soluble in their molten salts, *e.g.* sodium in sodium chloride, lead in lead chloride, silver in silver chloride and cadmium in cadmium chloride. The last mentioned system has been investigated carefully by several authors, firstly because the melting points of its components lie within temperatures which allow the system to be heated in pyrex glass tubes, and secondly, because the solubility of cadmium in molten cadmium chloride is rather high (about 0.18 mol. cadmium per mol. cadmium chloride).

At first these systems were investigated in connection with the electrolysis of molten salts. It was found that the deviations from Faraday's law in these processes were due to the solubility of the deposited metal in the molten salt (R. Lorenz).¹

When solutions of metals in molten salts are cooled, the mass solidifies and the metal comes out of solution. In this way dispersed systems are formed. In the system lead-lead chloride the solidified mass contains metal particles of colloidal dimensions (R. Lorenz and W. Eitel),² and the same happens in the system silver-silver chloride (latent photographic image), according to the ultramicroscopic investigations of these authors. The solidified system cadmium-cadmium chloride, however, is in many cases more coarsely dispersed; the metal particles in the solidified mass have microscopic dimensions, and can be extracted by mercury if the melt has been cooled slowly (Aten,³ confirmed by Hollens and Spencer),⁴ or if it has been quenched in carbon tetrachloride (Heymann and Friedlaender). If the molten system has been quenched in water, which is more effective, the cadmium particles have approximately colloidal dimensions (H. Terrey).⁵

It is, however, much more difficult to make a definite statement with regard to the nature of the molten systems. For a long time many investigators believed that the molten systems also contain—at least partially—metal particles of colloidal dimensions, and it was for this reason that the systems were described as "pyrosols" (Lorenz).

But several experimental results are not in concordance with this assumption. Aten has shown as early as 1910 that the dissolution of cadmium causes a considerable melting point depression of cadmium chloride. Later W. Eitel and B. Lange⁶ found by investigation in an

¹ R. Lorenz, *Z. anorg. Chemie*, 1895, 10, 88; *Z. Elektrochemie*, 1900, 7, 227; R. Lorenz and W. Eitel, *Pyrosols*, Leipzig, 1926.

² R. Lorenz and W. Eitel, *Z. anorg. Chemie*, 1915, 91, 46.

³ A. H. W. Aten, *Z. physik. Chemie*, 1909, 66, 641; 1910, 73, 578.

⁴ W. A. R. Hollens and J. F. Spencer, *J. Chem. Soc.*, 1934, 1062.

⁵ Private communication for which we are much indebted to Mr. H. Terrey, University College, London.

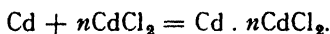
⁶ W. Eitel and B. Lange, *Z. anorg. Chemie*, 1928, 171, 168.

ultramicroscope, which permitted the systems to be heated, that the solutions of cadmium in cadmium chloride as well as those of lead in lead chloride do not contain particles of ultramicroscopic visibility, that is to say, no particles larger than 20×10^{-7} cm. Finally, E. Heymann and E. Friedlaender⁷ investigated the distribution equilibrium of cadmium between bismuth as one phase and cadmium chloride as the other. The concentration of cadmium in the metal phase was proportional to the concentration of cadmium in the salt phase. As cadmium forms monatomic solutions in bismuth (Heycock and Neville),⁸ this result proves, according to Nernst's distribution law, that the solutions of cadmium in cadmium chloride are true monatomic solutions. This conclusion was confirmed by an application of Nernst's method of solubility decrease to the system cadmium-cadmium chloride (as suggested by A. Magnus), where small amounts of bismuth were added to the cadmium phase (bismuth is insoluble in and does not react with cadmium chloride).

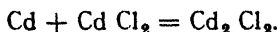
On the other hand, several authors had already recognised that strong chemical forces must exist between the dissolved metal atoms and the salt molecules (Lorenz, Hevesy and Wolff,⁹ Eitel and Lange, Heymann and Friedlaender). This is suggested by the fact that alkali chlorides, which form complex salts with lead chloride, decrease the solubility of lead in lead chloride, the secondary valencies binding the metal atoms with the lead chloride molecules being now occupied by the molecules of the added alkali chloride. Furthermore, the absorption spectrum of cadmium solutions in molten cadmium chloride must be completely different from that of cadmium vapour, the solutions having a dark brown colour, whereas the vapour is colourless.

We have to consider three possibilities :

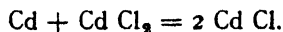
(1) The cadmium atoms, dissolved in cadmium chloride, are solvated by cadmium chloride molecules.



(2) The cadmium atoms react with cadmium chloride with the formation of a subchloride Cd_2Cl_2 .



(3) The cadmium atoms react with cadmium chloride with the formation of a subchloride CdCl .



The probability of the existence of a subchloride was especially emphasized by Hevesy and Loewenstein¹⁰ because of the analogous behaviour of the solutions of cadmium in cadmium chloride and of molten calomel when alkali salts are added. In the molten systems $\text{Cd}-\text{CdCl}_2$ and $\text{Pb}-\text{PbCl}_2$, alkali salts, added to the salt phase, generally produce a considerable decrease of the solubility of the metal (Lorenz and Appelberg,¹¹ Hevesy and Loewenstein). They also decrease the solubility of mercury in mercuric chloride or, in other words, produce the decomposition of mercurous chloride as well as of other mercurous salts. This analogy is very striking indeed.

⁷ E. Heymann and E. Friedlaender, *Z. physik. Chemie*, 1930, 148A, 177.

⁸ Heycock and Neville, *J. Amer. Chem. Soc.*, 1892, 61, 892.

⁹ Lorenz, v. Hevesy and Wolff, *Z. physik. Chemie*, 1911, 76, 732.

¹⁰ v. Hevesy and Loewenstein, *Z. anorg. Chemie*, 1930, 187, 266.

¹¹ Lorenz and Appelberg, *Z. anorg. Chemie*, 1903, 35, 36.

It seemed possible that measurements of the magnetic susceptibility might throw some light on this problem. The cadmium atom has two s -electrons in the O_I shell, the divalent cadmium ion has a complete N_{III} shell; both must be diamagnetic, whereas the monovalent Cd^+ ion with one odd electron will be paramagnetic. Thus, if the solutions of cadmium in molten cadmium chloride contain $CdCl$ in appreciable amount the system will be paramagnetic. If, however, the system consists of dimeric subchloride molecules Cd_2Cl_2 there will be no odd electron, and consequently the system will be diamagnetic. Finally, if the system contains no subchloride, but only solvated cadmium atoms $Cd \cdot nCdCl_2$, the system must be also diamagnetic.

Measurements of the solid systems have been made by Hollens and Spencer,⁴ showing these to be diamagnetic. This is very readily understood, for several authors have shown the solid to consist of a mixture of metallic cadmium and cadmium chloride.

The present paper is concerned with magnetic measurements of the molten systems. Investigations have been made on 7.6 per cent. and 9.7 per cent. solutions of cadmium in cadmium chloride. For reasons of the analogy between the cadmium and the mercury compounds some measurements with molten calomel were carried out as well. Magnetic investigations of other well-known systems of this type, *e.g.* $Pb-PbCl_2$, are, however, not promising because of the very small solubility of lead in lead chloride, and were therefore left out.

Experimental.

For the purpose of this investigation it is not necessary to have a high degree of accuracy, since it requires only about 2 per cent. of paramagnetic $CdCl$ to counteract the diamagnetism of the mixture of cadmium chloride and cadmium and to make the mass non-magnetic. A much smaller quantity is sufficient to give a measurable effect. This being so, it was decided to use a simple Gouy method with an estimated accuracy of 3-5 per cent. as being sufficient to show the presence of paramagnetic material in the mixture.

In the Gouy¹² method, the measurement is made by suspending a long uniform cylinder of the material from one arm of a sensitive weighing balance so that its lower end is in a position between the pole pieces of the magnet where the field is uniform and the upper end in a position where the field is negligible, and finding the force on the specimen by direct weighing when the field is applied.

The susceptibility is then given by the expression

$$F = \frac{1}{2}(k_1 - k_2)AH^2, \quad . \quad . \quad . \quad (1)$$

where F is the force, k_1 and k_2 are respectively the volume susceptibilities of the specimen and of the medium in which it is suspended, in this case air, A is the cross-section of the specimen and H is the field. The mass susceptibility is then given by

$$\chi = \frac{k_1}{\rho} \quad . \quad . \quad . \quad (2)$$

where ρ is the density. The densities in this investigation are those given by Aten,¹³ Lorenz and Frei,¹⁴ Klemm and Biltz,¹⁵ and Matsuyama.¹⁶

¹² Stoner, *Magnetism and Matter*, p. 81, London, 1934.

¹³ Aten, *Z. physik. Chemie*, 1910, **73**, 590.

¹⁴ Lorenz and Frei, *Z. physik. Chemie*, 1907, **61**, 468.

¹⁵ W. Klemm and W. Biltz, *Z. anorg. Chemie*, 1926, **152**, 240.

¹⁶ Matsuyama, *Sci. Rep. Tohoku*, 1929, **18**, 20.

The results of the measurements of the molten systems are given in Table III.

TABLE II.—CADMIUM CHLORIDE SOLUTIONS IN WATER.

Weight Per Cent.	$- \chi \times 10^6$ of Solution.	$- \chi \times 10^6$ of CdCl_2 .
13.5	0.680	0.422
21.7	0.650	0.398
46.4	0.570	0.391

The mixtures of cadmium in cadmium chloride were obtained by treating the molten salt with an excess of metallic cadmium, shaking or stirring for one hour, and quenching in carbon tetrachloride. The solidified mass contained the metal in microscopic particles which were easily redissolved in the salt when the mass was heated above the melting-point of the cadmium chloride ($568^\circ \text{C}.$).

TABLE III.—SUSCEPTIBILITIES OF THE MOLTEN SYSTEMS.

Substance.	Temp. $^\circ \text{C}.$	F in mg.	A in cm^3 .	$(k_1 - k_2)$ $\times 10^6$.	$\frac{\chi}{M}$ $\times 10^6$ 	ρ .	$\frac{\chi}{M}$ $\times 10^6$
Cadmium	20	19.0	0.396	1.534	1.505	8.65	0.17
	475	16.0	0.396	1.292	1.287	7.84	0.16
	600	15.6	0.396	1.259	1.256	7.67	0.16
	650	15.2	0.396	1.227	1.224	7.61	0.16
Cadmium chloride . . .	600	20.7	0.460	1.494	1.491	3.32	0.45
7.6 per cent. cadmium in * cadmium chloride . . .	600	12.2	0.270	1.445	1.442	3.36	0.43
	800	12.2	0.270	1.445	1.442	3.24	0.44
9.6 per cent. cadmium in * cadmium chloride . . .	600	20.7	0.461	1.436	1.433	3.38	0.42
Mercurous chloride (calomel) . . .	550	19.6	0.438	1.482	1.477	5.80	0.26
	580	20.0	0.438	1.512	1.507	5.68	0.27
Lead chloride . . .	600	20.5	0.444	1.529	1.526	4.72	0.32

* atomic per cent.

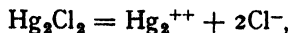
Discussion.

As a result of the measurements, it is certain that the solutions of cadmium in cadmium chloride are diamagnetic in the molten as well as in the solid state. Thus the existence of a subchloride CdCl has to be definitely excluded. Also, if the temperature is raised to $800^\circ \text{C}.$ there is practically no change in susceptibility, that is to say, there is no sign that a paramagnetic compound, for instance the endothermic subchloride CdCl , is formed when the temperature is raised.

On the other hand, the measurements do not exclude the existence of a bimolecular subchloride Cd_2Cl_2 , because such a substance would be diamagnetic. The existence of such a compound in the solutions of cadmium in molten cadmium chloride would provide an analogy with molten calomel which is also diamagnetic. It has to be remembered, however, that apart from the general analogy in the behaviour of cadmium halides and mercury halides, emphasized by Hevesy, there is no physical property which really proves the existence of a subchloride Cd_2Cl_2 in the solutions of cadmium in cadmium chloride. Although on the basis of

the magnetic measurements the existence of a subchloride Cd_2Cl_3 is as likely as that of a solvated cadmium atom $\text{Cd} \cdot n\text{CdCl}_2$ in the molten systems, the latter assumption is perhaps less hypothetical.¹⁷

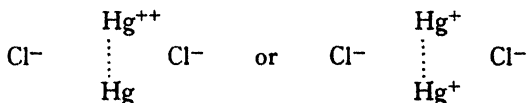
The results obtained with molten calomel are interesting, especially if compared with the measurements of the electric conductivity by Klemm and Biltz.¹⁸ The molten calomel is diamagnetic as well as the solid calomel,¹⁹ therefore the melt cannot consist of HgCl molecules or Hg^+ ions. It can only consist of Hg_2Cl_2 molecules; these must be dissociated to some degree into dimeric mercurous ions Hg_2^{++} and chlorine ions,



because the electric conductivity of the molten calomel is rather high (equivalent conductivity about 40), that is to say, of the order of magnitude of typical ionic melts. Mercuric chloride, however, has a very low electric conductivity (equivalent conductivity about 0.0025); thus it consists of molecules. Therefore the diamagnetism of the molten calomel cannot be due to a high degree of decomposition into mercury and mercuric chloride, because a solution of this metal in its salt would equally have a small conductivity.²⁰ It is known, however, that this decomposition takes place to some degree, but according to Klemm and Biltz does not exceed about 6 per cent., which is in accordance with our experiments.

The existence of Hg_2^{++} ions in the molten calomel has its analogy in the constitution of aqueous solutions of mercurous salts; it is very likely that these solutions contain mainly dimeric Hg_2^{++} ions (Ogg²¹).

In molten salts there certainly exist strong inter-ionic and intermolecular forces. Therefore the possibility of more complex configurations might be taken into account, for instance the existence of a loose complex such as



or probably intermediate configurations due to the exchange of electrons. We are indebted to Dr. E. Teller for having suggested these configurations to us. The presence of the chemically active mercury atom or Hg^+ ions might account for the weak binding of electrons which would give rise to the intense colour. Also the fact that the Hg^+ ions are present in pairs makes this configuration reconcilable with the appearance of diamagnetism. The considerable rise in electric conductivity (about ten thousand times), which occurs when we proceed from molten mercuric chloride to mercurous chloride by addition of mercury, would have its parallel in the fact that sodium atoms, dispersed in sodium chloride crystals, increase the electric conductivity by several powers of ten (Röntgen,²² Pohl²³).

¹⁷ For a discussion on the existence of a cadmium subchloride in the gas phase see S. Barrat and A. R. Bonar, *Phil. Mag.*, 1930, 9, 519.

¹⁸ Klemm and Biltz, *Z. anorg. Chemie*, 1926, 152, 225.

¹⁹ Lowry and Gilbert, *Nature*, 1929, 123, 85.

²⁰ According to Aten (*loc. cit.*) dissolution of cadmium in cadmium chloride produces a decrease of electric conductivity.

²¹ Ogg, *Z. physik. Chemie*, 1898, 27, 285.

²² A. Röntgen, *Ann. Physik. Chemie*, 1921, 64, (4), 1.

²³ R. Pohl, *Naturwiss.*, 1926, 14, 215.

Possibilities, such as described above, would be a kind of an intermediate state between the "solvated atom" and the "subchloride." The existence of an analogous configuration in the solutions of cadmium in cadmium chloride may equally be taken into account. In this case the electrolytic conductivity of the pure cadmium chloride is already so high that no further increase takes place when cadmium metal is dissolved in the melt. The small decrease in conductivity which has been observed by Aten¹⁸ might be due to the fact that Cd^{++} . . . Cd and Cd^+ . . . Cd^+ have a smaller mobility than Cd^{++} .

A short remark may be made in regard to the difference in susceptibility between the solid and the molten salts. The rise in susceptibility which is found when CdCl_2 is molten is interesting in that it is greater than that experienced when organic molecules melt. Some additional experiments with lead chloride gave a similar result. It is known that these salts become ionised in the molten state from electric conductivity data. It is to be expected that ionisation should raise the susceptibility and this may well be the explanation of the rise observed in these experiments. The fact that the value for cadmium chloride from aqueous solution lies between the values for solid and molten cadmium chloride appears to confirm this assumption, but the solution of cadmium chloride in water is very complex as it is partially electrolytically and partially hydrolytically dissociated and, therefore, little stress can be laid on this result.

Summary.

1. Magnetic measurements with solutions of cadmium in molten cadmium chloride and with molten calomel have been made. In no case has paramagnetism appeared. Thus a subchloride CdCl is definitely excluded. The probability of either a subchloride Cd_2Cl_3 or an atomic solution of cadmium in cadmium chloride is discussed as well as a more complex configuration.

2. A comparison of the magnetic properties with the electric conductivity of molten calomel leads to the assumption that it consists of Hg_2Cl_2 molecules which are to some degree dissociated into Hg_2^{++} and chlorine ions; also in this case a more complex configuration is taken into consideration.

3. There is an unexpected large rise in diamagnetic susceptibility when CdCl_2 , PbCl_2 and Hg_2Cl_2 melt.

We wish to express our thanks to Professor F. G. Donnan, F.R.S., for his constant encouragement and interest.

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THE INFLUENCE OF THE ELECTRODE SURFACE ON ANODIC PROCESSES.

BY O. J. WALKER AND J. WEISS.

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Two types of anodic process have been largely investigated in electrolytic reactions, *viz.* (1) the evolution of oxygen (which involves the phenomenon of oxygen overvoltage), and (2) the oxidation of various inorganic and organic ions and molecules. In general, both types of reaction may occur at the anode during the electrolysis of any given aqueous solution. Such processes have been investigated both experimentally and theoretically in great detail.¹ More recently, the mechanism of electrode processes has been discussed from the points of view of statistical and of quantum mechanics.² Further reference to this will be made later on.

In a recent series of studies on electrolytic oxidations Glasstone and Hickling³ have proposed a new general theory for the mechanism of anodic oxidation, which contradicts the views of Foerster and his school¹ and the similar views maintained by one of us⁴ in some recent papers. Since many of their assumptions are open to criticism, it seems necessary to reconsider the question of electrolytic oxidation.

We can first deal briefly, however, with the main arguments of Glasstone and Hickling's theory. They state that H_2O_2 is formed as the primary reaction product by the combination of hydroxyl radicals on the surface of the anode. From the purely experimental standpoint this view is highly improbable, since the anodic formation of H_2O_2 has never been detected even in traces.⁵ In the homogeneous gaseous system and in solution there is no direct evidence for the recombination reaction $2\text{OH} = \text{H}_2\text{O}_2$. In the presence of a surface, however, it is known with certainty, as was first shown by Bonhoeffer and Pearson⁶ and confirmed by Rodebush and Wahl,⁷ that this recombination never takes place, but rather the reaction $2\text{OH} \rightarrow \text{H}_2\text{O} + \text{O}$. The formation of H_2O_2 in the glow discharge electrolysis may occur somewhere in the gas phase or at the liquid surface, as has been shown by Haber and Klemenc,⁸ Rodebush and Wahl⁷ and others.⁹ It is by no means certain that the H_2O_2 formed in this case is always due to the recombination of OH radicals, but even so it is not permissible to compare the conditions in a glow discharge (at 500-1000 volts) with those prevailing at a metal anode dipping into an aqueous solution.

¹ Cf. Foerster, *Elektrochemie d. wässrigen Lösungen*.

² J. A. V. Butler, *Trans. Faraday Soc.*, 1924, **19**, 734; R. W. Gurney, *Proc. Roy. Soc.*, 1931, **134A**, 137.

³ Glasstone and Hickling, Part VI., *J.C.S.*, 1934, 1878.

⁴ S. N. Shukla and O. J. Walker, *Trans. Faraday Soc.*, 1931, **27**, 35, 722.

⁵ Except under unusual conditions of low temperature, *e.g.*, at -40°C ., *cf.* Riesenfeld and Reinhold, *Ber.*, 1909, **42**, 2977.

⁶ Bonhoeffer and Pearson, *Z. physikal. Chem.*, 1931, **14B**, 1.

⁷ Rodebush and Wahl, *J. Chem. Physics*, 1933, **1**, 696.

⁸ Haber and Klemenc, *Z. Elektrochem.*, 1914, **20**, 485.

⁹ W. R. Cousins, *Z. physik. Chem.*, 1929, **4B**, 440.

The only experimental evidence put forward by Glasstone and Hickling for the intermediate formation of H_2O_2 in such varied processes as the anodic oxidation of thiosulphates, of sulphites, and of acetates, is that the addition of salts of Pb, Ag, Mn, Co, etc., brings about a marked change in the anode process. This is attributed by them to a catalytic decomposition of the H_2O_2 , for which these salts are known to act as catalysts. As, however, H_2O_2 is certainly not formed (under the conditions of their experiments), it is necessary to account in some other way for the experimental results obtained on adding the above-mentioned metallic salts.

Many examples are known where, in the electrolysis of solutions containing these metal salts, layers of metal oxides are formed at the anode, the surface of which is thereby completely changed.¹ It seemed very likely, therefore, that in the experiments of Glasstone and Hickling the change in the electrode process was connected with the change of the anode surface. Accordingly some of their experiments were repeated to demonstrate that also under their experimental conditions oxide layers are formed on the anode.

Experimental.

For this purpose we selected the electrolysis of potassium acetate solutions described in Glasstone and Hickling's most recent paper.* In this reaction the effect of the added salts in changing the anode process is very marked. Their experimental conditions were reproduced in all essential points. Solutions of potassium acetate, containing free acetic acid, to which other metallic acetates had been added, were electrolysed at room temperature in a glass vessel with a smooth platinum wire cathode and a smooth platinum foil anode (1×1 cm.). The cathode and anode compartments were separated by a thick plug of glass wool, and the solution in the anode compartment was stirred rapidly. Previous to use, the anodes were cleaned with hot HCl, HNO_3 , water, and then heated to redness. The electrolysis was allowed to proceed (as in the experiments of Glasstone and Hickling) in each case for 15 minutes at 0.5 amps, corresponding to a total passage of 450 coulombs at a C.D. of 0.25 amps per sq. cm.

The results are summarised in the following table :—

TABLE I.

No. of Expt.	Concn. of CH_3COOK gm. mols./litre.	Concn. of CH_3COOH gm. mols./litre.	Nature and Concn. of Added Acetate gm. mols./litre.	Condition of Platinum Anode (Initially Bright and Smooth) at End of Electrolysis.
1	1.0	1.0	None	Bright and smooth
2	1.0	1.0	$(CH_3COO)_2Pb$ 0.01 M	Thick deposit of chocolate brown PbO_2
3	1.0	1.0	$(CH_3COO)_2Mn$ 0.1 M	Marked brown deposit of manganese oxide
4	1.0	1.0	CH_3COOAg 0.013 M	Black deposit
5	1.0	1.0	$(CH_3COO)_2Co$ 0.1 M	No visible deposit. Electrolyte changed from pink colour to brown

In experiments 2-4, an obvious darkening of the bright anode surface commenced soon after starting the electrolysis, and a considerable deposit

was left on the anode at the end of the experiment. It is clear, therefore, that a marked change occurs in the nature of the anode surface on the addition of Pb, Mn, and Ag acetates in the electrolysis. Even in the case of cobalt a very thin film of oxide is most probably formed, and its formation is made more likely by the fact that considerable oxidation of the cobaltous salt took place, as shown by the darkening of the electrolyte.

Discussion of Experiments.

These results show that under the experimental conditions used by Glasstone and Hickling a definite change in the anode surface takes place through the formation of oxide layers.

It is well known that the nature of the surface is an important factor in influencing the reactions which may occur at an electrode. For example, Regelsberger¹⁰ found that chromium salts, which are not oxidised at platinum anodes, are readily oxidised on the addition of small amounts of lead salts, which form a PbO_2 layer on the anode. Platinum electrodes with (electrolytically formed) cobalt, nickel and iron oxides, show a quite different behaviour to platinum itself in anodic oxidations. Müller and Spitzer¹¹ found the same kind of behaviour even in cases where the oxide layers are not visible to the eye. These observations are supported by some experiments of Tafel,¹² who showed that in general even monomolecular layers can change the nature of an electrode.

Theoretical Discussion.

We shall now discuss in more detail the two types of reaction referred to above, *viz.* (1) the liberation of oxygen at the anode, and (2) anodic oxidation processes.

In general there exists a potential barrier between the metal surface (of the anode) and the ions in the adsorbed layer. According to the Pauli-Sommerfeld theory we have in a metal quasi-free electrons which obey the Fermi-Dirac statistics. Electron transfer can take place into the metal from the adsorbed negative ions (or molecules) on the surface of the anode through the potential barrier. According to quantum mechanics this electron transfer takes place mainly between electron levels of the same energy. Therefore the following relation must hold:—

$$\Phi + V_a > E_{\text{ion}} + H_{\text{ion}}.$$

In this expression

Φ = work function of the metal electrode.

V_a = applied positive potential which increases the work function to $\sim (\Phi + V_a)$.

E_{ion} = electron affinity of the adsorbed negative ion which is transferring its electron to the metal.

H_{ion} = hydration energy of the negative ion.

This is similar to the expression developed in more detail by Gurney³ who, however, did not take into account that the reacting ions are in the adsorbed state. Topley and Eyring¹³ have recently pointed out that in

¹⁰ Regelsberger, *Z. Elektrochem.*, 1899, **6**, 308.

¹¹ Müller and Spitzer, *Z. Elektrochem.*, 1905, **11**, 917.

¹² Tafel, *Z. physikal. Chem.*, 1900, **34**, 193.

¹³ Topley and Eyring, *Nature*, 1934, **133**, 292.

the case of the discharge of hydrogen ions on a metallic cathode the adsorption energies must be involved. Therefore we have

$$\Phi + V_a > E_{\text{ion}} + H_{\text{ion}} - \Delta A \quad (1)$$

where $\Delta A = A_R - A_I$, A_I being the adsorption energy of the ion and A_R the adsorption energy of the radical formed by its discharge. In general, ΔA will always be positive as $A_R > A_I$.

From expression (1) the well-known influence of the electrode surface, which we have emphasised above, can easily be seen. Two material constants of the metal are involved, one being the work-function Φ of the metal surface (under the given conditions), and the other the term ΔA , which not only differs for different metals, but also may be different for different surfaces of one and the same metal. It is difficult to discuss the influence of ΔA alone, as both ΔA and Φ are dependent in a similar way on the properties of the surface.

Oxygen Evolution at the Anode.

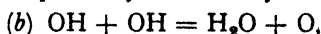
In the case of oxygen liberation we have to consider the discharge of OH^- ions at the surface, according to



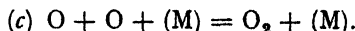
The direct decomposition of water on the anode may also become important (particularly in the case of low OH^- ion concentration) according to¹⁵



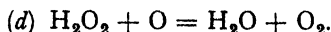
These reactions are most probably followed by



and finally,



The rate determining reaction is in general reaction (a) or (a'). Reference has already been made to the fact that reaction (b) takes place (on the metal surface). Further evidence for the formation of oxygen atoms by this process is obtained from the experiments of Tanatar,¹⁶ confirmed by one of us,¹⁷ on the catalytic decomposition of H_2O_2 on an anode, according to



Furthermore, Butler and Armstrong¹⁸ were able to show that in the case of noble metals, such as gold and platinum, a monomolecular layer of oxygen atoms is present on the metallic surface during anodic polarisation.

We can see from expression (1) that in order that electron transfer may occur (and an appreciable current flow) we must increase the work function by increasing the applied positive potential V_a . This additional

¹⁵ In this case expression (1) takes the form :

$$\Phi + V_a > D_{\text{H}_2\text{O}} + I_{\text{H}} - \Delta A$$

where $(\Phi + V_a)$ has the same meaning as above.

$D_{\text{H}_2\text{O}}$ = dissociation energy of H_2O into an H atom and an OH radical.

I_{H} = ionisation potential of the H atom.

$\Delta A \sim A_{\text{OH}}$ (adsorption energy of the OH radical).

¹⁶ Tanatar, *Ber.*, 1903, **36**, 199.

¹⁷ Weiss, *in preparation*.

¹⁸ Butler and Armstrong, *Proc. Roy. Soc.*, 1932, **137A**, 604.

positive potential, which is really the overvoltage, will be different for different metals and various surfaces, as we have pointed out above. We may refer here to the measurements of Coehn and Osaka,¹⁹ and of Foerster and Piguet²⁰ on oxygen overvoltage at different anode surfaces, and to the paper of Müller and Spitzer (*loc. cit.*), who showed that the oxides of Fe, Co, and Ni have low overvoltages of about the same value as those of the metals themselves.

According to the previous considerations, one should expect the overvoltage to decrease with increasing work function of the (metal) electrode and with increasing adsorption power for the OH radical. As oxide layers in some form are always present on the surface, the work functions of the metals under electrode conditions must not be compared with those of the pure metals, but will in general be modified. It is well known²¹ that the work function is influenced by gases adsorbed on the metal surface. Adsorbed oxygen usually increases the work function and the overvoltage is thereby decreased. On the other hand, the rough or spongy surface with the higher adsorption power for the OH radical (ΔA very large) should have the lower overvoltage, in agreement with experiment.

Anodic Oxidation Processes.

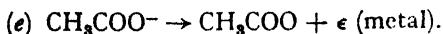
We shall now consider the case where we have oxidation of anions taking place as well as oxygen evolution. In this case we must compare the expression for the discharge of OH⁻ ion with that for the discharge of another anion (A⁻) present in the electrolyte.

$$\Phi + V_a \begin{cases} > E_{\text{OH}^-} + H_{\text{OH}^-} - \Delta A_{\text{OH}} \\ > E_{\text{A}^-} + H_{\text{A}^-} - \Delta A_{\text{A}}. \end{cases}$$

Φ may differ for the two expressions. If one can assume this difference to be small, then, in general, conditions will be more favourable for the discharge of any anion present than for OH⁻ ion, as the electron affinity of the latter exceeds the electron affinities of other anions ($E_{\text{OH}^-} > E_{\text{A}^-}$). Also,²² for the common anions $H_{\text{A}^-} < H_{\text{OH}^-}$. The primary discharge of OH⁻ will be possible only when ΔA_{OH} is relatively large ($\Delta A_{\text{OH}} > \Delta A_{\text{A}}$).

A distinction should therefore be made between (a) electrodes with high overvoltage, and (b) electrodes with low overvoltage. So that we should expect anodes of high oxygen overvoltage (*e.g.* smooth platinum) to favour the primary discharge of any anion, whereas on anodes of low overvoltage (*e.g.* platinised platinum and metallic oxides) the OH⁻ ion will be discharged in preference. The resulting OH radicals may then take part in chemical oxidations on the electrode.

For instance, in the case of the anodic oxidation of acetates we have to expect the following processes. On smooth platinum there will occur mainly the direct discharge of acetate ions according to



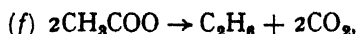
¹⁹ Coehn and Osaka, *Z. anorg. Chem.*, 1903, **34**, 86.

²⁰ Foerster and Piguet, *Z. Elektrochem.*, 1904, **10**, 714.

²¹ Cf. Hughes and Du Bridge, *Photoelectric Phenomena*, 1933.

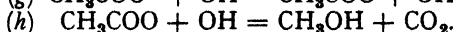
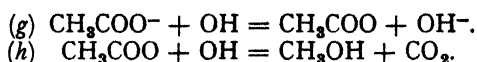
²² K. F. Herzfeld, *Kinetische Theorie der Wärme* (Vieweg, 1926).

If there are no other reactive molecules present the free radicals then react



giving mainly ethane and carbon dioxide (Kolbe reaction). Practically no oxygen is evolved under these conditions.

In the case of surfaces of low overvoltage, however, such as platinised platinum, cobalt, nickel, iron, PbO_2 , MnO_2 , Ag_2O , we get mainly primary discharge of OH^- ions. The resulting reactive OH radicals are able even at low concentrations (*i.e.* at potentials lower than that at which appreciable oxygen evolution occurs) to react chemically with the electrolyte according to



It is clear that at an anode of low overvoltage, the OH^- ion is easily discharged and reactions (g) and (h) take place (along with some oxygen liberation).

On the other hand, if the electrode is sufficiently "poisoned," *e.g.* by $\text{Hg}(\text{CN})_2$, KCN, brucine, etc.,³ the overvoltage for the discharge of OH^- rises and the Kolbe reaction becomes prominent again.

The oxidation of the acetate to give CH_3OH and CO_2 in processes (g) and (h) (Hofer-Moest reaction) takes place (on electrodes of low overvoltage) at a considerably lower potential than the Kolbe reaction (on electrodes of high overvoltage). This can be well understood as in reactions (g) and (h) there is a depolarising influence due to the electrolyte, which lowers the potential.²³ It therefore follows that under the conditions in question the Kolbe and Hofer-Moest reactions are taking place on electrode surfaces of different behaviour.

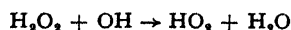
The same distinction between anodes of high and low oxygen overvoltage is apparent in all other anodic processes.²⁴

The considerations which we have dealt with in the case of acetates hold similarly in the case of the other reactions investigated by Glasstone and Hickling. For instance, the $\text{S}_2\text{O}_3^{2-}$ ion is either discharged directly giving $\text{S}_4\text{O}_6^{2-}$ or else is oxidised to sulphate.

Also, in the electrolysis of sulphite solutions the effect of anodic pre-polarisation in favouring²⁵ the formation of $\text{S}_2\text{O}_8^{2-}$ (by the combination of directly discharged SO_3^- ions) is readily explained by the well-known increased overvoltage on pre-polarised platinum anodes.¹

The effect of the addition of the metallic salts is the same for all these anodic oxidations studied by Glasstone and Hickling. The effect decreases in the order $\text{Pb}, \text{Ag} > \text{Mn} > \text{Cu}, \text{Co}, \text{Fe}$. This is the same

²³ This depolarising influence on the oxygen potential is always to be expected if substances are added which are able to react quickly with the OH radical. This is indicated by the experiments of Haber, and of Haber and Grinberg, who have shown that H_2O_2 when added to the anode electrolyte lowers the anodic potential very markedly (*Z. anorg. Chem.*, 1898, 18, 37; 1906, 51, 361) by acting as a strong depolariser. The H_2O_2 then reacts either according to reaction (d) or directly with the OH radicals



as in the catalytic decomposition of H_2O_2 investigated by Haber and Weiss (*Proc. Roy. Soc.*, 1934, 147, 332).

²⁴ Foerster, *loc. cit.*

²⁵ Glasstone and Hickling, *J. Chem. Soc.*, 1932, 2345, 2800.

order as the case of formation of oxide layers found in our experiments, which all have a low overvoltage for discharge of OH^- .

Summary.

(1) The two types of anodic process, *viz.* (1) the evolution of oxygen (which involves the phenomenon of oxygen overvoltage) and (2) oxidation of various inorganic and organic ions and molecules, have been discussed.

(2) The influence of the addition of metallic salts (*e.g.*, of Pb, Mn, Ag, Co) to the electrolyte to be oxidised has been studied with reference to the work of Glasstone and Hickling.

(3) The conditions for the discharge of anions and the breaking up of molecules at the anode have been considered, and the electron transfer to the metal anode has been discussed.

In conclusion, we wish to thank Mr. B. Topley for valuable discussions.

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THE PERIODIC GROUPS OF NON-HYDRIDE DI-ATOMS.

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I. Principles of Classification.

This communication purposes to extend and give definite form to proposals made rather more than three years ago by the author,⁴ with reference to the classification of non-hydride di-atoms. The method has already been partly carried into practice,⁷ but up to the present no complete table has been published, showing cases thus far not experimentally realised. Classification assumes particular significance in cases where it becomes possible to predict spectroscopic magnitudes and general properties with considerable confidence. The present paper is therefore concerned also with rules which have been found useful for this purpose. The author has pointed out elsewhere the advantages of the procedure, and has applied it to the estimation of undetermined constants, so that this point need not be further elaborated.

The fundamental Periodic Group Table is presented in Table IV.

Experimental data are largely lacking for di-atoms containing elements of the rare earths, Mendeljéeff's Group VIII. and the radioactive series. These are therefore omitted from the present discussion, but they should be capable of inclusion in the scheme with the advent of further experimental information. Account is taken, with the above exceptions, and omitting the inert gases, of 54 atoms from atomic number 3 (lithium) to 83 (bismuth), all the possible combinations in pairs being taken into account. The atoms may be considered in their spectroscopic periodic group classification, as formulated by the author,⁸ according to their assignments of *s*, *p* and *d* electrons in incomplete

groups. The general convention is adopted of underlining the symbols of atoms containing incomplete groups of d electrons, since such groups confer distinctive characteristics to compounds.

Three more or less independent variables of a di-atom XY must be combined in all possible ways, as follows: (a) the completed electron system of the atom X ; (b) the completed electron system of the atom Y ; (c) the "shared" electron system derived from the two incomplete electron groups of X and Y , denoted by e_X and e_Y , respectively. (a) and (b) form the "non-bonding" groups, and define the period, whilst (c) defines the group of the di-atom. The group number n is equal to the sum of e_X and e_Y . For a given n , different values of e_X and e_Y lead to the sub-groups within groups, as explained below.

It becomes more important than might appear at first sight to decide in which order the symbols shall be written in defining a di-atom. Convention has already settled that, in general, the more metallic atom shall be placed first. The following rule will follow this method: "The atom contributing the smaller number of electrons to the shared group is placed first in writing a symbol; if the electron contributions are equal, the atom having the greater nuclear charge is placed first." This may be called the "Convention Principle."

Considering the group of shared electrons (c), it is found possible to include all the di-atoms for which the necessary spectroscopic constants are recorded by the simple supposition that *not more than seven electrons are derived from one atom* in forming the group. This may be termed the "Restriction Principle," leading directly to thirteen periodic groups II. to XIV., from $n = 2$ (e.g. LiK) to $n = 14$ (e.g. ICl). The 54 atoms concerned may be combined in pairs in ${}^{54}C_2 + 54 = 1,485$ ways. These are distributed amongst the groups as shown at the foot of Table I.

TABLE I.—SUBDIVISION OF THE GROUPS OF NON-HYDRIDE DI-ATOMS.

Periodic Group of XY.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.	X.	XI.	XII.	XIII.	XIV.	Total.
n	2	3	4 4	5 5	6 6 6	7 7 7	8 8 8 8	9 9 9	10 10 10	11 11	12 12	13	14	
e_X	1	1	1 2	1 2	1 2 3	1 2 3	1 2 3 4	2 3 4	3 4 5	4 5	5 6	6	7	
e_Y	1	2	3 2	4 3	5 4 3	6 5 4	7 6 5 4	7 6 5	7 6 5	7 6	7 6	7	7	
Sub-group	s	a	b s	b a	c b a	c b a	d c b s	c b a	c b s	b a	b s	a	s	
Number of Sub-groups	1	1	2	2	3	3	4	3	3	2	2	1	1	28
Number of Di-atoms	36	64	100	128	164	184	212	176	148	112	84	49	28	1485

The largest number of sub-groups occurs in the central group where n is even, since, on account of the Restriction Principle, there is here the greatest choice of sets of electron contributions, *viz.* (i) 4, 4; (ii) 3, 5; (iii) 2, 6; (iv) 1, 7; as the values of e_X and e_Y respectively (four sub-groups). It is convenient to distinguish the symmetrical case (i) by the symbol "s," whilst (ii), (iii) and (iv) are labelled "b," "c" and "d" respectively, denoting progressively decreasing symmetry of the e_X 's and e_Y 's, or, which generally amounts to the same thing in practice, of

TABLE III.

PERIOD MATRIX									
1	2	3	4	5	6	7	8	9	10
11	12	13	14	15	16	17	18	19	20
21	22	23	24	25	26	27	28	29	30
31	32	33	34	35	36	37	38	39	40
41	42	43	44	45	46	47	48	49	50
51	52	53	54	55	56	57	58	59	60
61	62	63	64	65	66	67	68	69	70
71	72	73	74	75	76	77	78	79	80
81	82	83	84	85	86	87	88	89	90
91	92	93	94	95	96	97	98	99	100
101	102	103	104	105	106	107	108	109	110
111	112	113	114	115	116	117	118	119	120
121	122	123	124	125	126	127	128	129	130
131	132	133	134	135	136	137	138	139	140
141	142	143	144	145	146	147	148	149	150
151	152	153	154	155	156	157	158	159	160
161	162	163	164	165	166	167	168	169	170
171	172	173	174	175	176	177	178	179	180
181	182	183	184	185	186	187	188	189	190
191	192	193	194	195	196	197	198	199	200
201	202	203	204	205	206	207	208	209	210
211	212	213	214	215	216	217	218	219	220
221	222	223	224	225	226	227	228	229	230
231	232	233	234	235	236	237	238	239	240
241	242	243	244	245	246	247	248	249	250
251	252	253	254	255	256	257	258	259	260
261	262	263	264	265	266	267	268	269	270
271	272	273	274	275	276	277	278	279	280
281	282	283	284	285	286	287	288	289	290
291	292	293	294	295	296	297	298	299	300
301	302	303	304	305	306	307	308	309	310
311	312	313	314	315	316	317	318	319	320
321	322	323	324	325	326	327	328	329	330
331	332	333	334	335	336	337	338	339	340
341	342	343	344	345	346	347	348	349	350
351	352	353	354	355	356	357	358	359	360
361	362	363	364	365	366	367	368	369	370
371	372	373	374	375	376	377	378	379	380
381	382	383	384	385	386	387	388	389	390
391	392	393	394	395	396	397	398	399	400
401	402	403	404	405	406	407	408	409	410
411	412	413	414	415	416	417	418	419	420
421	422	423	424	425	426	427	428	429	430
431	432	433	434	435	436	437	438	439	440
441	442	443	444	445	446	447	448	449	450
451	452	453	454	455	456	457	458	459	460
461	462	463	464	465	466	467	468	469	470
471	472	473	474	475	476	477	478	479	480
481	482	483	484	485	486	487	488	489	490
491	492	493	494	495	496	497	498	499	500
501	502	503	504	505	506	507	508	509	510
511	512	513	514	515	516	517	518	519	520
521	522	523	524	525	526	527	528	529	530
531	532	533	534	535	536	537	538	539	540
541	542	543	544	545	546	547	548	549	550
551	552	553	554	555	556	557	558	559	560
561	562	563	564	565	566	567	568	569	570
571	572	573	574	575	576	577	578	579	580
581	582	583	584	585	586	587	588	589	590
591	592	593	594	595	596	597	598	599	600
601	602	603	604	605	606	607	608	609	610
611	612	613	614	615	616	617	618	619	620
621	622	623	624	625	626	627	628	629	630
631	632	633	634	635	636	637	638	639	640
641	642	643	644	645	646	647	648	649	650
651	652	653	654	655	656	657	658	659	660
661	662	663	664	665	666	667	668	669	670
671	672	673	674	675	676	677	678	679	680
681	682	683	684	685	686	687	688	689	690
691	692	693	694	695	696	697	698	699	700
701	702	703	704	705	706	707	708	709	710
711	712	713	714	715	716	717	718	719	720
721	722	723	724	725	726	727	728	729	730
731	732	733	734	735	736	737	738	739	740
741	742	743	744	745	746	747	748	749	750
751	752	753	754	755	756	757	758	759	760
761	762	763	764	765	766	767	768	769	770
771	772	773	774	775	776	777	778	779	780
781	782	783	784	785	786	787	788	789	790
791	792	793	794	795	796	797	798	799	800
801	802	803	804	805	806	807	808	809	810
811	812	813	814	815	816	817	818	819	820
821	822	823	824	825	826	827	828	829	830
831	832	833	834	835	836	837	838	839	840
841	842	843	844	845	846	847	848	849	850
851	852	853	854	855	856	857	858	859	860
861	862	863	864	865	866	867	868	869	870
871	872	873	874	875	876	877	878	879	880
881	882	883	884	885	886	887	888	889	890
891	892	893	894	895	896	897	898	899	900
901	902	903	904	905	906	907	908	909	910
911	912	913	914	915	916	917	918	919	920
921	922	923	924	925	926	927	928	929	930
931	932	933	934	935	936	937	938	939	940
941	942	943	944	945	946	947	948	949	950
951	952	953	954	955	956	957	958	959	960
961	962	963	964	965	966	967	968	969	970
971	972	973	974	975	976	977	978	979	980
981	982	983	984	985	986	987	988	989	990
991	992	993	994	995	996	997	998	999	1000

TABLE IV.—The Periodic Groups of Non-Hydride Di-Atoms.

11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54	55	56	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86	87	88	89	90	91	92	93	94	95	96	97	98	99	100
11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54	55	56	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86	87	88	89	90	91	92	93	94	95	96	97	98	99	100
11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54	55	56	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86	87	88	89	90	91	92	93	94	95	96	97	98	99	100
11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54	55	56	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86	87	88	89	90	91	92	93	94	95	96	97	98	99	100
11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54	55	56	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86	87	88	89	90	91	92	93	94	95	96	97	98	99	100
11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54	55	56	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86	87	88	89	90	91	92	93	94	95	96	97	98	99	100
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11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54	55																																													

the two nuclear charges. In an odd-numbered group, the most symmetrical sub-group evidently has $e_x + 1 = e_y$, and is denoted by "a," further departures from symmetry being denoted by "b" and "c." Such considerations applied to all the groups lead to 28 sub-groups symmetrically distributed about the central group VIII., as in Table I. A given di-atom is readily assigned to its appropriate sub-group; thus, AlN ($e_x = 3$, $e_y = 5$) belongs to VIIIb, and so on.

Proceeding next to take account of the non-bonding groups, it is necessary to have an abbreviated symbolism, as in table II.

TABLE II.—SYMBOLS FOR NON-BONDING GROUPS.

Non-bonding Group.	Symbol.	Number of Electrons.
K^2	K	2
K^2L^8	L	10
$K^2L^8M^8$	M	18
$K^2L^8M^{18}$	\bar{M}	28
$K^2L^8M^{18}N^8$	N	36
$K^2L^8M^{18}N^{18}$	\bar{N}	46
$K^2L^8M^{18}N^{18}O^8$	O	54
$K^2L^8M^{18}N^{32}O^8$	\bar{O}	68
$K^2L^8M^{18}N^{32}O^{18}$	$\bar{\bar{O}}$	78

In the Table, K and L denote completed K and L rings respectively, M denotes the partial completion of the third quantum group with 8 electrons, \bar{M} (read M-bar) the completion of the group with 18 electrons, and similarly for N, \bar{N} ; O, \bar{O} . The symbol $\bar{\bar{O}}$ (read O-dot) signifies the filling-in of the fourth quantum group to its maximum of 32 electrons.

The next task carried through in the Period Matrix (Table III.) consists in combining these non-bonding groups in all possible ways. The symbol KK denotes, for instance, two completed K rings associated with each nucleus. The letter "S" after a number, showing the total number of electrons in a completed group, indicates that two non-bonding groups are the same; this is further shown by shading. Where a given number of total non-bonding electrons may be obtained in more than one way, further letters "A," "B" and "C" are used to denote successively decreasing symmetry of the non-bonding groups.

The construction of Table IV.* is based upon combining each period derived from the period matrix with each possible group and sub-group derived from the separate electron contributions to the shared group. Since three variables are involved, the table is essentially three-dimensional. The Period Matrix is taken as a basal horizontal plane, and the nine successive sections marked KK to $K\bar{\bar{O}}$, LK to $L\bar{\bar{O}}$. . . are raised vertically from the plane in their appropriate places: then all di-atoms of the same sub-group occur at the same vertical height above the matrix plane. The horizontal plane of a given di-atom defines its group and sub-group, and its position in the plane, as referred to the basal matrix, defines its period. Thus BeO may be represented by KK-VIIIc, AlP by LL-VIIIb, AgS by $\bar{N}L$ -VIIc, and so on. Each di-atom has only one possible place under the chosen conditions.

The three-dimensional effect may be conveniently achieved by cutting out the nine sections and pasting the lettering at the foot of each on the corresponding lettering of the Period Matrix.

* *Corrigenda*.—In period $\bar{L}\bar{M}$, group IXa, read SiAs for SiAg.

II. General Consideration of the Table.

In a given period of Table IV. (vertical columns KK, KL . . .), each compartment of the period represents a different group, according to the numbering shown on the left-hand edges. Members of different sub-groups of the same group are placed within the same compartment, in order downwards of progressively increasing symmetry of the electron contributions of the separate atoms. The spaces in the table arise from the Convention Principle, and from the omission of the rare earths and elements after bismuth in atomic number. Thus, the space at the top of the KL period is empty; it might contain LiNa, but this is listed as NaLi (by the Convention Principle) and therefore appears in the LK period, and so on.

Molecules having an equal number of extranuclear electrons have been termed "isoelectronic molecules," or "isosteres." The above definition is too general, however: for example, it would be meaningless to include SbO and CuZn (59 extranuclear electrons). It is necessary in practice to restrict the word "isostere" to a given group or sub-group in the classification. It becomes desirable to subdivide into three types, for which the terms *orthostere*, *metastere* and *parastere* are suggested.

Orthosteres are members of a given period and group, having different sub-groups. The number of sub-groups in a group is the maximum number of orthosteres in a group (see Table I.), the greatest possible number occurring in group VIII. For example, in the KK period, in group VIII., we have LiF, BeO, BN and CC, which may be expected to show certain resemblances as well as gradations of properties in the series. It may be noted that with increasing symmetry of the nuclear charges, orthosteres tend to pass from polar to homopolar types.

Closer resemblances still may be expected to occur in the case of *metasteres*, which are members of the same sub-group but of "reversed" period (for example, LK and KL). Metasteres arise, for given e_x 's and e_y 's, by interchanging the two non-bonding groups; hence there is very great similarity in structure. For example, for $e_x = 4$, $e_y = 6$, Ke_xLe_y and Le_xKe_y correspond to CS and SiO respectively in group Xb, and it is found that their spectroscopic constants are closely alike (section IV., case (C)). The close resemblance between CP and SiN has been independently observed.²

Parasteres are members of the same sub-group, having different non-bonding groups. Referring to the Period Matrix (Table III.), the same total number of non-bonding electrons occurs in the periods designated by the same numbers but having different letters; for example, 20S and 20B; 64A, 64B and 64C; and so on. Some examples are given in section IV. under case (D). This subdivision of isosteres turns out to be less important than the other two.

It becomes possible to predict a certain number of properties of diatoms not yet investigated by consideration of their position in the group table with reference to other members, in a somewhat similar fashion to Mendeljéeff's predictions for eka-silicon, etc. In making such comparisons, it is important, however, to consider not only the position in the table, but also the structural nature of the di-atom in question. Thus, where d electrons are present in the incomplete group of either of the constituent atoms, the resulting di-atom will fall into a different class, corresponding to Mendeljéeff's A sub-groups in the atomic groups III. to VII. Since every di-atom of this kind is shown clearly marked by

underlining in Table IV., very little risk of unsuitable comparisons need arise. In a group of orthosteres, the presence of di-atoms of this kind may be expected to modify the general regularities observed in other cases. For example, in the MK-VIII group KF, CaO, ScN and TiC occur together: it may be anticipated that certain characteristic differences will be manifest in the two halves of the group. It should also be borne in mind that caution is necessary in comparing cases where either or both of the constituent atoms have 8 electrons in one case and 18 in the other in their outermost completed groups. Since the bar above the period symbol denotes this case quite clearly, again no confusion need arise.

Using underlining and bars as suggested, nine types of di-atoms may arise, obtained by combining one of \bar{X} , \bar{X} and \underline{X} with one of \bar{Y} , \bar{Y} and \underline{Y} in all possible ways.

In the three following sections, a study is made, in connection with three fundamental rules, of the changes in certain spectroscopic constants which occur accompanying structural changes in di-atoms of related type. As a guiding principle, it is found that *an increase or decrease in r_e corresponds to a decrease or increase respectively in the magnitudes usually defined by ω_e , $\omega_e x_e$, D and B_e* , whilst α remains approximately constant in a given period. This may be conveniently referred to as the "Direction Principle."

III. The Rule of Asymmetry.

The Rule of Asymmetry may be stated as follows: *When non-hydride di-atoms of similar type are compared in their ground states, increasing asymmetry is accompanied by decreasing fundamental vibration frequency, and vice versa.*

The rule may be extended to other spectroscopic constants by means of the Direction Principle at the end of the preceding section. We may consider applications of the rule to 4 cases, lettered (A) to (D), as below.

Case (A). Di-atoms XY where either X or Y is fixed.—If one atom is fixed, and the other increased in weight without alteration in group, thereby decreasing the symmetry, the fundamental vibration frequency may be expected to decrease. A few examples are appended:

Metallic Di-atom.	ω_e (cm. ⁻¹).	Halide Di-atom.	ω_e	Oxide Di-atom	ω_e .
NaNa NaK HNaRb HNaCs } Group II.	159.2 123.3 (100)(ω_0) (96)(ω_0)	BeF MgF HCaF HSrF HBaF } Group IXc	1265.6 690.8 586.7 500.1 468.9	BO AlO HScO HYO HLaO } Group IXb	1885.4 977 971.6 852.5 811.6

The symbol H indicates that the value of the frequency stated was obtained by measurement of a band-head.

A similar gradation occurs in a series of elementary di-atoms XX of the same group:

An interesting point arises in connection with the very small decrease in fundamental frequency in passing from AlO to ScO (see table above).

Di-atom	ClCl	BrBr	II	Group XIV
$\omega_e(H)$	564.9	323.9	214.3	

Scandium is the first element where "inner

building" occurs by addition to the 3-quantum group of d electrons, and it appears that these two facts may very well be connected together.

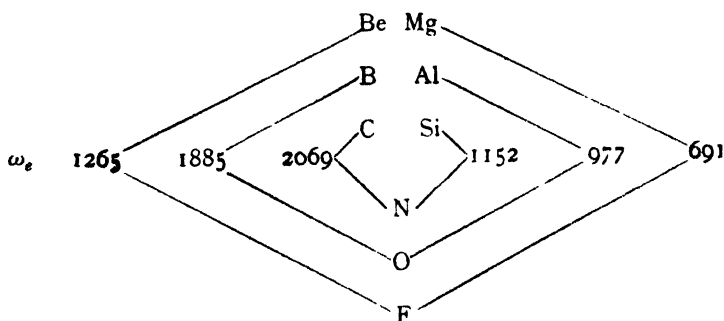
It might be thought that the Rule of Asymmetry would prove to be without exception, so far as case (A) is concerned, since an increase of reduced mass, other things being more or less equal, occurs in passing along a group. Experiment does not quite confirm this view. Increases of frequency apparently occur in the following cases:—

Di-atom.	$\omega_e(\text{H})$	Di-atom.	$\omega_e(\text{H})$	Di-atom.	$\omega_e(\text{H})$
MgO	722	SrO	651.9	AgCl	343.6
CaO	852	BaO	665.5	AuCl	382.8

The fundamental frequency increases in the series $\text{BeO} \rightarrow \text{BO} \rightarrow \text{CO}$, but this turns out to be no exception to the rule.

The frequencies also increase in the series $\text{MgO} \rightarrow \text{AlO} \rightarrow \text{SiO}$ (see discussion in section V.).

Case (B). Orthosteres.—No exception has been recorded to the rule that, in a group of orthosteres, there is an increase in fundamental frequency with increasing symmetry of distribution of the nuclear mass. The fundamental frequencies in the ninth group of the KK and LK periods give the inequalities $\text{CN} > \text{BO} > \text{BeF}$; $\text{SiN} > \text{AlO} > \text{MgF}$. This may be represented as in the following scheme:—



The constants for this group of six di-atoms being largely determined, the values are reproduced here, as given by Jevons.²¹

Period.	Group.	Di-atom.	ω_e	$\omega_e \times \epsilon$	D	B_e	α	r_e
KK	IXc	BeF	1265.6	9.12	(6.0)	1.4793	0.01685	1.357
	IXb	BO	1885.4	10.71	(6.6)	1.780	0.017	1.199
	IXa	CN	2068.8	13.18	7.09	1.8904	0.0173	1.169
LK	IXc	MgF	H690.75	3.95	—	—	—	(1.838)*
	IXb	AlO	977	7.0	—	0.6386	0.00575	1.614
	IXa	SiN	1151.68	6.56	—	0.7280	0.00567	1.568

These numbers illustrate the tendency of the first four magnitudes given to increase with each other, and to decrease with r_e , in accordance

with the Direction Principle. Moreover, α is approximately constant within a given group, whilst varying discontinuously from one period to another. Careful examination of the existing data shows that α is fairly constant through a given period, with a certain tendency to reach larger values in the middle groups. This tendency is much more noticeable in the case of ω_e , and the other constants (see Fig. 1 and discussion below).

Further inequalities in ω_e values in accordance with the rule are observed in the following cases: $\text{ScO} > \text{CaF}$; $\text{YO} > \text{SrF}$; $\text{LaO} > \text{BaF}$; $\text{NN} > \text{CO}$; $\text{CC} > \text{BeO}$; and so on.

The di-atom ions of the first period (KK) appear at first sight to provide an exception to the rule. Thus the following inequalities occur in ω_e : $\text{CO}^+ > \text{BO}$; $\text{NN}^+ > \text{CN}$; $\text{NO} > \text{OO}^+$. It becomes clear, however, that in dealing with charged di-atoms, another factor may enter into consideration. The charged di-atom has a total nuclear charge one unit greater than that carried by the extranuclear electrons, so that the repulsion between the nuclei will be more felt, with a tendency to increase the internuclear distance and decrease the equilibrium frequency, as compared with the corresponding neutral di-atom, in spite of an increase in symmetry of nuclear mass. This effect will operate, therefore, in the direction opposite to that suggested by the rule, and will presumably be felt most as the absolute values of the nuclear charges increase. The results are then entirely in accord with theory; an increase in symmetry from BO to CO^+ and from CN to NN^+ results, in agreement with the rule, in an increased equilibrium frequency, whilst from NO to OO^+ , with larger nuclear charges, the nuclear charge effect opposes the increase of symmetry of masses, and the order of change in the two previous cases is reversed. The change in the opposite direction is very slight, and is nearly overcome by the symmetry effect.

The spectroscopic constants of the six cases discussed are set out in the following scheme:—²¹

Period.	Group.	Di-atom or Ion.	ω_e .	$\omega_e x_e$.	D .	B_e .	α .	r_e .
KK	IXb	BO	1885.4	10.71	(6.6)	1.780	0.017	1.199
		CO^+	2212	15.17	7.1	1.97	—	1.11
	IXa	CN	2068.8	13.18	7.09	1.8904	0.0173	1.169
		NN^+	2206.8	16.04	6.8	1.922	0.02	1.113
	XIa	NO	1906.5	14.424	(6.1)	1.675	0.0178	1.146
		OO^+	1876.4	16.53	6.15	1.610	0.009	1.14

It becomes possible to make a certain number of simple predictions with a considerable amount of confidence. From the present rule concerning orthosteres, it may be expected that the fundamental frequencies of the following di-atoms will be found to be less than the stated amounts (in cm^{-1}): $\text{LiF} < 1487.45$ (BeO); $\text{BF} < 2167.4$ (CO); $\text{CF} < 1906.5$ (NO); $\text{NF} < 1584.9$ (OO); and so on. The upper and lower limits for BN will be 1641.55 (CC) and 1487.45 (BeO) respectively, and so on. The di-atom TiN will be expected to have a (slightly?) smaller frequency than 1151.68 (SiN), by the rule of asymmetry (case A), whilst it will be greater than 971.55 (ScO) (case B). The rule is observed to enable rough estimates of numerous magnitudes to be made, for other spectroscopic magnitudes may be easily included by the principles set forth.

Case (C). Metasteres.—It has often been pointed out that many of the physical properties of CO and NN, for example, exhibit close resemblance; yet such groups are not chemically alike, and it is here observed, since they stand in orthosteric relation, that their spectroscopic constants, instead of being approximately the same, show a characteristic gradation according to the Rule of Asymmetry. When, however, metasteres are compared, a much closer relation should be observed; a point which has apparently so far escaped notice. The symmetry properties of NS and PO, for example, are closely alike; their structures differ only in the transference of one unit of positive charge from one nucleus to the other. The extranuclear systems must be practically identical, so that their *chemical properties should be very nearly the same*.

When the Rule of Asymmetry is applied to metasteres, the close resemblance in symmetry properties would imply a similar correspondence in spectroscopic numbers, with small variations due to slight differences in distribution of mass. It appears that, as a working guide, we may assume that for metasteres, in general, the asymmetry effect is almost absent, and *the fundamental frequency is subject to small changes depending on the "reduced masses" μ of the pair of di-atoms, tending to increase somewhat as μ decreases, and vice versa*. The present rather meagre data enables comparison to be made between four pairs of metasteric di-atoms, as follows :—²¹

Period.	Group.	Di-Atom.	$\mu (\times 10^{24})$.	ω_e .	$\omega_e x_e$.	D .	B_e .	α .	r_e .
\overline{NM} \overline{MN}	VIII _d	AgBr	75.70	H 250.2	0.83	2.6	—	—	—
		CuI	69.43	H 265.13	0.76	—	—	—	—
KL LK	IX _a	CP	14.27	1239.67	6.75	6.9	0.7958	—	1.56
		SiN	15.39	1151.68	6.56	6.2	0.7282	0.00567	1.57
KL LK	X _b	CS	14.40	H1282.5	6.00	—	—	—	1.56
		SiO	16.80	H1240.5	5.95	—	0.724	0.005	1.51
KL LK	XI _a	NS	16.11	H1220	7.75	—	—	—	(1.47)
		PO	17.41	H1235	7	—	—	—	(1.46)

The spectroscopic constants of the above metasteres, taken in pairs, show a definite tendency to become closely alike, and the member of a pair having the higher reduced mass tends to have the lower fundamental vibration frequency. This is reversed in the case of NS and PO, but here the ω_e 's lie close together, so that, since the measurements are on band-heads, the exception may be apparent rather than real. The r_e estimates enclosed in brackets are values calculated by the modified Morse Rule.⁶ It may be anticipated that the spaces in the above scheme will become filled by numbers closely alike, the inequalities being governed by the Direction Principle. It may be noted that the polar di-atoms AgBr and CuI appear to give as good general agreement with these principles as, for example, the homopolar pair CS and SiO.

It becomes possible to prepare a table showing data for one of a pair of metasteres where the other has not yet been experimentally examined. For this purpose, it is convenient to divide the cases into Classes I. and II., the latter class containing cases where, in each pair, one of the two di-atoms contains an atom having d electrons in its incomplete group. The resulting scheme is given below :—²¹

Class.	Period.	Group.	Di-atom.	Data for Meta-steres.	ω_e	$x_e \omega_e$	D.	B_e	α	r_e
I	KM	VIIIId	LiBr	CuF	H 620.59	3.842	—	—	—	—
	LM	VIIIId	NaBr	CuCl	H 417.02	1.64	—	—	—	—
	LN	VIIIId	NaI	AgCl	H 343.6	1.163	3.11	—	—	—
	KL	VIIIc	BeS	MgO	H 722	5.96	—	—	—	—
	KL	IXc	BeCl	MgF	H 690.75	3.95	—	—	—	(1.838)
	KL	IXb	BS	AlO	977	7.0	—	0.6386	0.00575	1.614
	LK	Xc	AlF	BCl	—	—	—	(2.25)	—	(1.0)
	LM	Xb	SiSe	GeS	H 575.8	1.80	(5.65)	—	—	—
	KN	Xb	CTe	SnO	H 813.5	5.5	(3.66)	—	—	—
	KL	XIb	CCl	SIF	H 865	4.55	—	0.2904	—	2.259(r_e)
	LN	XIb	SiI	SnCl	H 352.6	1.2	—	—	—	—
	KN	XIa	NTe	SbO	H 824.3	5.9	—	—	—	—
II	KM	IXb	BCr	ScO	H 971.55	3.95	—	—	—	—
	KN	IXb	BMo	YO	H 852.5	2.45	—	—	—	—
	KM	Xb	CCr	TiO	H 1008.12	4.519	—	0.53377	0.00275	1.617
	KN	Xb	CMo	ZrO	H 936.7	3.50	—	—	—	—
	KM	XIa	NCr	VO	H 1014	6	—	—	—	—
	MK	XIII	CrF	OMn	H 841.7	5.05	—	—	—	—

Case (D). Parasteres.—So far as the meagre experimental results show, the Rule of Asymmetry is inapplicable to parasteres. Thus CuBr(56S-MM) and AgCl(56B-NL) in Group VIIIId, each having 64 electrons, show values of $\omega_e(H) = 314.1$ and 343.6 respectively, with a small increase with increasing asymmetry. Similarly, the series of diatoms SrBr(64A-NM), CaI(64B-MN) and BaCl(64C-OL) in Group IXc, each having 73 electrons, have values of $\omega_e = 215$, 241 and 288 respectively. There is also very probably an increase in fundamental frequency from NaNa to KLi.

The explanation of this anomaly may be found as follows. Parasteres differ fundamentally from orthosteres and metasteres, in that they do not strictly fulfil the condition of being "di-atoms of similar type." The fact that the total number of electrons is identical appears fortuitous, and without structural importance. For example, the non-bonding groups in CuBr and AgCl are $28 + 28$ and $46 + 10$ respectively; the groups are different, and the coincidence of the totals may be regarded as accidental. The Rule of Asymmetry is therefore inapplicable. On the other hand, all the above results may be explained in terms of changes in reduced mass, which, for example, increases from AgCl (43.58) to CuBr (57.80), with a corresponding decrease in fundamental frequency, and similarly for the other quoted cases.

Justification is hereby found for the author's subdivision of isosteres into three sets, for each is distinct from the others, and for parasteres the structural relations are more apparent than real.

IV. The Rule of Means.

The Rule of Means may be stated as follows: *The internuclear distance of a non-hydride di-atom XY in its ground state is approximately the arithmetic mean of the internuclear distances of the di-atoms XX and YY in ground states.* A corresponding statement may, with certain limitations, be made for fundamental equilibrium frequencies (section B below).

(A) The Additivity of Atomic Radii obtained from Band Spectra.

Pauling²⁷ has shown that *for covalent compounds* the inter-atomic distances are approximately additive, allowance being made according as the bonds involved are single, double or triple. The rule placed above is implied for covalent links, the internuclear distance of ICl being found to be very near the mean of the values for II and ClCl. (In this connection, it may be observed that the widely quoted assignment of the atomic radius of fluorine from the band spectrum of FF as $r(\text{F}) = 0.64$ Å.U. is uncertain.⁹) Rodebush²⁹ has stated that atomic radii obtained from band spectra are additive, the deviations in general being less than 0.01 Å.U., *even where the molecule involves a mixed type of bonding* (italics of the present author). This extension from the purely covalent cases considered by Pauling to those in which at least some measure of polarity is present assumes significance.

The rule as applied to di-atoms in general has a larger limit of possible error than that assigned by Rodebush. Sometimes the signs may be wrong, as observed in the inequalities $r_e(\text{OO}) > r_e(\text{NN})$, $r_e(\text{SiO}) < r_e(\text{SiN})$, $r_e(\text{CO}) < r_e(\text{CN})$. On the other hand, we find, $r_e(\text{FF}) > r_e(\text{OO})$, $r_e(\text{BeF}) > r_e(\text{BeO})$, in conformity with the rule. The differences

$$r(\text{F}) - r(\text{O}) = 0.666 - 0.602 = 0.06$$

and

$$r_e(\text{BeF}) - r_e(\text{BeO}) = 1.357 - 1.328 = 0.03 \text{ Å.U.},$$

are closely alike, so the extension of the rule to polar di-atoms (BeF and BeO) seems justified. Polar cases may be distinguished by the condition: $e_x \neq e_y$. Some results are collected together in the table, which shows comparison between results obtained by the Rule of Means, the modified Morse rule, and experiment.

Di-atom.	Period and Group.	Sub-group.	Equilibrium Internuclear Distance (Å.U.).			Deviations.	
			Calculated.		Observed.		
			Rule of Means.	Morse-Clark.			
			(1).	(2).		(3).	(1)-(2).
PN	LK-X	s (e _x = e _y)	1.48	1.45 ⁸	1.49 ¹¹	+0.03	-0.01
SO	LK-XII		1.52	1.49 ⁸	1.49 ²¹	+0.03	+0.03
ICI	NL-XIV		2.32	—	2.31 ²¹	—	+0.01
CN	KK-IX	a (e _x + 1 = e _y)	1.20	1.15 ⁸	1.17 ²¹	-0.05	-0.03
NO	KK-XI		1.15	1.15 ⁸	1.15 ²¹	0.00	0.00
CP	KL-IX		1.58	1.51 ⁸	1.56 ^{2, 18}	+0.07	+0.02
CS	KK-X	b(e _x + 2 = e _y)	1.57	1.47 ⁸	1.56 ¹²	+0.10	+0.01
Average Deviations (irrespective of sign)						0.04	0.02

The average deviations of estimates of internuclear distance made by the Rule of Means in the tested cases are of the order 0.03 Å.U., whether judged by experiment or by values derived from the modified Morse Rule.

The di-atoms in the table are arranged in order of increasing asymmetry of e_x and e_y , commencing with three symmetrical cases of sub-group *s* (PN, SO, ICl), followed by three less symmetrical di-atoms of sub-group *a* (CN, NO, CP), and by the unsymmetrical di-atom CS of sub-group *b*. So far as the figures show, there is no definite increase in error with decreasing symmetry and increasing polarity. Again, extension of the rule to the more general case appears justified by the results. The internuclear distance of SS is taken* as 1.840 Å.U.

If the applicability of the Rule of Means is assumed as at least an approximate and working guide, it is possible to estimate the internuclear distance of any one of the three of types XX, XY, YY, so long as values for the other two are known. We may estimate the internuclear distance of PS, for example, as the mean of the experimental values of $r_e(\text{PP}) = 1.856^{10, 1}$ and $r_e(\text{SS}) = 1.840$ Å.U., giving $r_e(\text{PS}) = 1.85$ Å.U. Alternatively, we may start with $r_e(\text{BeO}) = 1.328$ and $r_e(\text{OO}) = 1.204$, giving $r_e(\text{BeBe}) = 1.45$ Å.U.; or, taking $r_e(\text{BeF}) = 1.357$ and $r_e(\text{FF}) = 1.331$ (modified Morse Rule), we obtain $r_e(\text{BeBe}) = 1.38$ Å.U., whence the mean value $r_e(\text{BeBe}) = 1.42$ Å.U. is reached. Similarly, from $r_e(\text{BO}) = 1.199$ and $r_e(\text{OO}) = 1.204$, the estimate for $r_e(\text{BB})$ is 1.19 Å.U., and so on. By a second application of the rule, $r_e(\text{BeB})$ may be obtained from the mean of the values for BeBe and BB, and similarly in like cases. It may happen that such use of the rule may not always lead to very accurate estimates, but, since the errors in the tested cases prove distributed between positive and negative, either they will be in opposite directions and tend to neutralise, or they will add together in the two steps. Even in the latter case, however, an error probably not greater than about 0.2 Å.U. might be involved.

It is evidently possible to estimate the internuclear distances of a considerable number of di-atoms within the limits of applicability of the rule, and it would take a good deal of space to show all the results. It will be convenient to prepare a table of estimated atomic contributions to internuclear distances in di-atoms. Any pair of values may then be added together to give the estimate according to the present method. The results, shown in Table V., are given to three decimal places, but the nearest second figure only should be used in assigning a value for a di-atom by addition of the separate contributions.

TABLE V.—ATOMIC CONTRIBUTIONS TO INTERNUCLEAR DISTANCES
(GROUND STATES) (Å.U.).

(*M*, modified Morse equation used; *D*, internuclear distance of XX halved;
R, obtained by use of Rule of Means).

Atom.		Atom.		Atom.		Atom.		Atom.	
Li-3	1.335 <i>D</i>	O-8	0.602 <i>D</i>	Na-11	1.535 <i>D</i>	S-16	0.920 <i>D</i>	K-19	1.955 <i>D</i>
Be-4	0.709 <i>R</i>	F-9	0.666 <i>MD</i>	Mg-12	1.173 <i>MR</i>	Cl-17	0.992 <i>D</i>	Tl-22	1.015 <i>R</i>
B-5	0.597 <i>R</i>	—	—	Al-13	1.012 <i>R</i>	—	—	Br-35	1.140 <i>D</i>
C-6	0.654 <i>D</i>	—	—	Si-14	0.962 <i>R</i>	—	—	I-53	1.330 <i>D</i>
N-7	0.547 <i>D</i>	—	—	P-15	0.928 <i>D</i> ¹⁰	—	—	Pb-82	1.316 <i>R</i>

According to Table V., for example, the internuclear distance of NS will be expected to be about $0.547 + 0.920 = 1.47$ Å.U. Taking the

* *Vide* Badger, R. M., *Physic. Rev.*, 1934 (ii.), 46, 1025.

atoms in pairs, 190 di-atoms are involved, for most of which experimental information as to internuclear distance is at present lacking.

The values show the usual periodicity of an atomic volume curve, with a minimum in each period. It is possible to calculate the internuclear distances of all di-atoms of KK, KL, LK and LL periods, and to demonstrate the characteristic periodicity of the numbers. The details are communicated elsewhere.⁸

The fact that the lithium and iodine atoms make approximately equal contributions is noteworthy. Comparison between spectroscopic and crystal data is made in section VI.

The conclusion is reached that, within the limits of applicability of the rule of means, each atom of a non-hydride di-atom makes an approximately constant contribution to internuclear distance. This result is reminiscent of W. L. Bragg's Law of Additivity of atomic radii in crystals, and embodies an extension of Mecke's principle, mentioned below, that radicals retain their dimensions in compounds. Indeed, starting with a list of atomic sizes, it is possible to deduce results for di-atoms as outlined above, and then to extend to more complicated radicals and molecules.

Mecke²⁵ has stated that "radicals are bricks which retain their dimensions in their stable compounds; the nuclear separations as they are deduced from the spectroscopy of diatomic molecules can thus be used in the investigation of complicated molecules with more atoms." Thus an important extension of the results described in this section may be possible.

(B) Application of the Rule of Means to Equilibrium Vibration Frequencies.

In the case of fundamental vibration frequencies, the Rule of Means respecting di-atoms of type XX, XY and YY may be applied approximately, with the following two restrictions: (1) The di-atom XY must belong to a *symmetrical* sub-group (II, IVs, VI, VIIIs, Xs, XII, XIV); (2) The fundamental frequencies of XX and YY must not differ too greatly.

The limitation to symmetrical sub-groups could hardly have been discovered without a knowledge of the present method of classification.

The equilibrium frequencies for di-atoms of the type XX (taken from Jevons' table) are all derived from measurements on band heads, except in the case of OO, where a question mark appears after the figure. The values are: LiLi 351.6, OO 1584.9, NaNa 159.2, SS 727.4, ClCl 564.9, KK 92.6, BrBr 323.9, and II 214.3 cm.⁻¹. The following rounded figures provide a basis for comparison between the Rule of Means and experiment, so far as data are available:—²¹

Period.	Group.	Di-atom.	Equilibrium Frequency.		Percentage Error.
			Calc.	Obs.	
MK	II	KLi	H 223	H207(ω_0)	—
ML	II	KNa	H 126	H123.3	+2.2
LK	XII _s	SO	H1156	1123.7	+2.9
NL	XIV	ICl	H 390	H384.6	+1.4
NM	XIV	IBr	H 269	H267.3	+0.6
Mean Percentage Error					+1.8

The agreement between calculated and experimental numbers appears generally satisfactory. It is observed that the rule works about as well for a metallic di-atom (KNa) as for homopolar di-atoms (ICl and IBr) at the extremes of the periodic groups. The greatest error occurs for SO where the ω_e 's of OO and SS differ considerably. It may be noted, however, that all the errors are positive, with an average of 1.8 per cent. In making the approximate predictions of the following table, therefore, the directly calculated figures are also shown reduced by this amount :—

Period.	Group.	Di-atom.	Equilibrium Vibration Frequency (Calc.).	
			Rule of Means.	Rule of Means (Reduced).
LK	II	NaLi	H256	H251
ML	XIV	BrCl	H444	H436

In accordance with anticipation, it proves unsafe to predict the vibration frequency of PN as the mean of NN (2359.6) and PP (779.3), since the values deviate greatly. The unreduced Rule of Means gives H1570 for PN (reduced value H1541), as against the experimental figure 1337.2 cm.⁻¹.^{11, 15} The relatively low fundamental frequency of PN corresponds to its weaker stability as compared with NN.

V. The Rule of Periodicity.

It is possible to state the Rule of Periodicity in the following special form: *Fundamental equilibrium frequencies of di-atoms are periodic group functions, varying in a characteristic way such that their values reach a maximum within each period.* The rule may be made more general by inclusion of other spectroscopic constants.⁸ In the case of equilibrium nuclear separations, the values show a minimum within each period, by the Direction Principle.

Fig. 1 shows the variation of fundamental frequencies in the KK and LK periods so far as the data permit, the

data for the two periods being plotted on different scales. Approximations are denoted by the use of brackets. It is observed that the

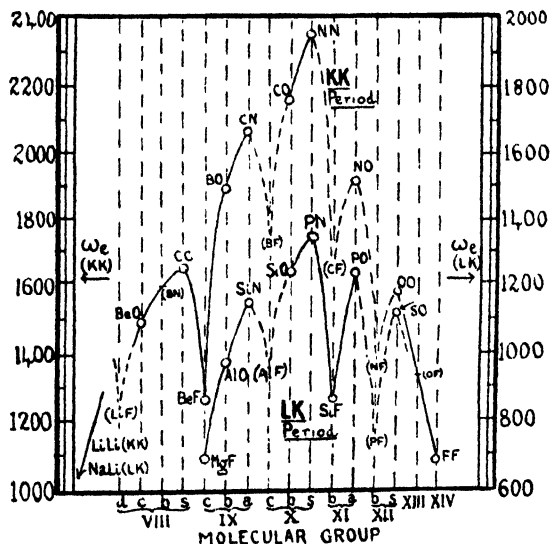
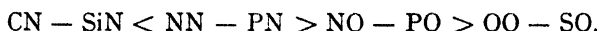


FIG. 1.—The Periodicity of Fundamental Frequencies.

curves sweep upwards through each group containing sub-groups, the positions of the maxima rising as far as group Xs, and then falling off again. There is insufficient data to enable the part of the curve before group VIII. to be drawn, but it probably continues in the same way, with continually decreasing maxima as far as group IVs. Since the equilibrium frequencies of LiLi and NaNa are evidently less than those of their partners FF and ClF at the far ends of their respective periods, the general form of the curve is an ascent from group II. to group Xs, afterwards falling off again, but never reaching the original value. The curve within groups II. to XIV. in the KK and LK periods is therefore unsymmetrical, the maximum occurring after the centres of the periods have been passed.

It becomes possible, by interpolation, to state that the equilibrium nuclear frequencies of BN and OF may be expected to lie at about 1,600 and 1,335 wave-numbers respectively.

The general form of the two curves is about the same, but it is observed that their maxima tend to approach each other on each side of group Xs. Thus, in respect of fundamental frequencies, the following inequalities may be observed :



Let us consider the change of fundamental frequency in a given group through different periods. The "period number" is the number of the column or row in which the period occurs in the matrix (Table III.). For example, the KL period is number 1 in the vertical series of periods from KL to OL, whilst it is number 2 in the horizontal series of periods from KK to KO, and so on. Fig. 2 is constructed to show changes in the logarithm of fundamental frequencies with vertical period numbers. (The distinction between vertical and horizontal has no absolute significance: it refers only to the convention adopted in constructing the period matrix.) Reference to Fig. 2 shows that the fundamental frequencies in the neighbourhood of group X tend to occupy the highest parts of the diagram, in accordance with the rule of periodicity. In fact, the figure divides itself roughly into three sections, the uppermost of which contains the oxides and nitrides, the middle the halides, and the lowest the intermetallic compounds. If the hydrides had been inserted, they would have occupied the space above the uppermost curve. This is in agreement with earlier observations on the Raman effect whereby, other things being equal, hydrides tend to have the highest frequencies, whilst compounds with triple, double and single bonds fall successively in this order.⁴ To this statement may now be added that the inter-metallic compounds tend to lie lower still.

The equilibrium vibration frequencies tend to fall with increasing period number, but the amount of fall varies with the kind of electronic rearrangement involved. It appears, so far as the available data go, that the effect of "inner building" in the transition series, as previously noted, is to introduce a much smaller change than usual, as the change of slope between AlO and ScO and between TiO and ZrO indicates. The data are generally insufficient for any satisfactory interpolations to be made.

Matayuma²³ has observed that the logarithms of the vibration frequencies of di-atoms XX in their ground states are in practically linear relation with atomic weights of X for a given atomic group, the series OO,

SS, SeSe, TeTe giving a line lying higher than that of FF, ClCl, BrBr, II, which in turn lies higher than that of LiLi, NaNa, KK, RbRb, CsCs. This is in accordance with the present results, which are, however, expressed in a somewhat different way.

The characteristic regions of Fig. 2 mentioned above may be roughly

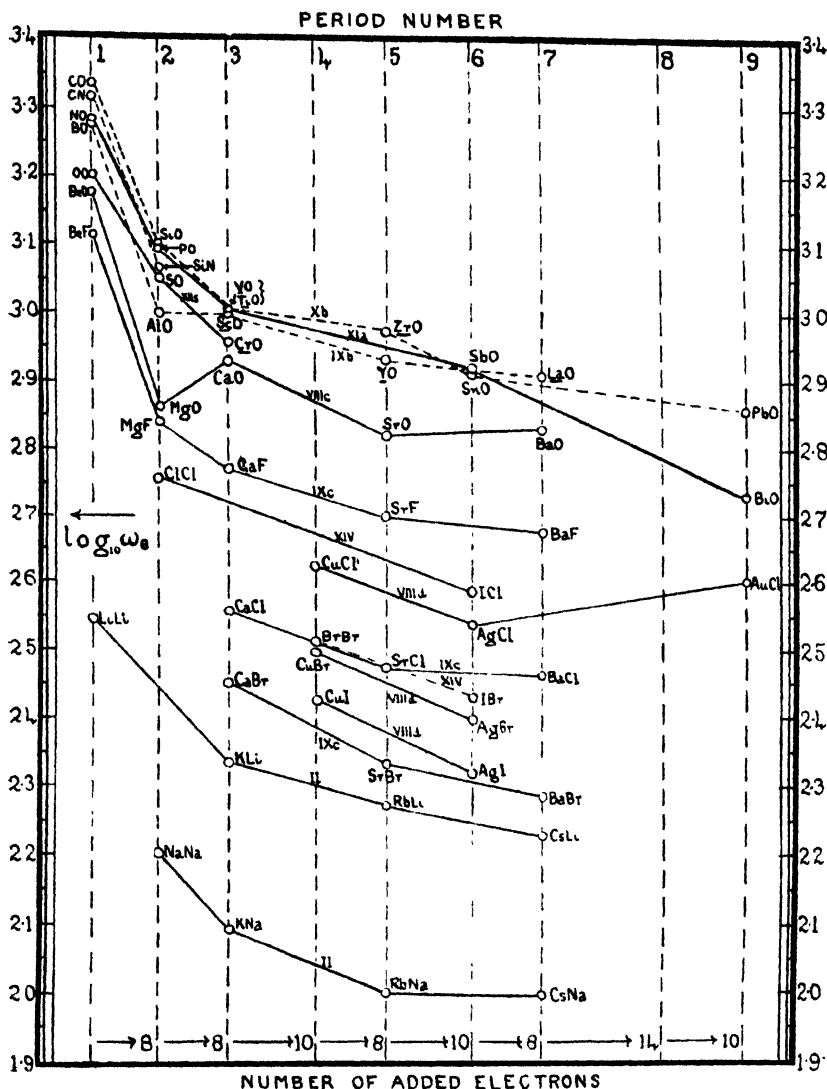


FIG. 2.—Variation of the Logarithm of Fundamental Frequency with Period Number.

designated as those of triple and double, single and metallic linkages. It is clear that, in the author's proposed classification, di-atoms which have metallic linkages will tend to occur in the earlier numbered groups, those with single bonds in the higher numbered groups, whilst those with double and triple linkages are in the intermediate groups. The rule derived from

the Raman Effect is thus brought into relation with the Rule of Periodicity.

It is possible, however, to go a little further, and to offer some suggestions as to the underlying cause of the phenomenon indicated by the rule. In Fig. 3, a few cases of di-atoms XY are considered in periods, where Y

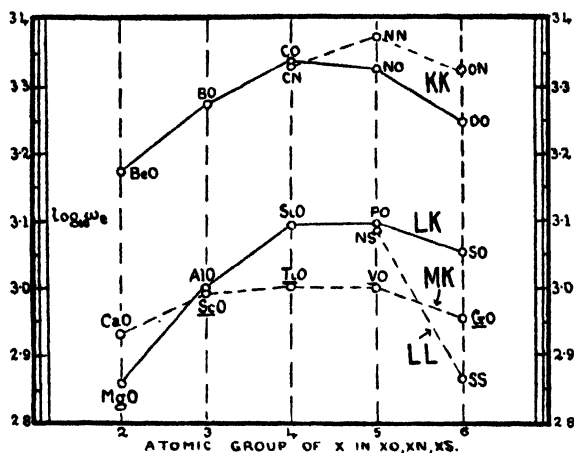


FIG. 3.—The Periodicity Rule in the case of Logarithms of certain Fundamental Frequencies.

is fixed, being O, N or S. The logarithm of the fundamental frequency is shown in relation to the atomic group of X. Let us consider the series from BeO to OO, the maximum lying at CO with its triple bond (see section XI.). There appear to be two oppositely directed influences at work. First, with increasing symmetry of the nuclear masses from BeO to OO, the fundamental frequency may be expected to increase; on the other hand, by case (A) of section VII., with increasing nuclear charge of X whilst Y remains constant, the frequency should decrease. The asymmetry of the nuclear masses being greatest in BeO, it may be expected that the asymmetry effect will operate and cause a rise in frequency; after CO, however, the effect of increasing nuclear mass of X makes itself felt. Thus the result may be explained by two different applications of the Rule of Asymmetry (section III.).

A similar explanation cannot be used to account for the rising portion of the curve from MgO to SiO. If we represent the nuclear masses of X and Y by x and y respectively, we may take the function $(x \sim y)/(x + y)$ as a measure of nuclear mass asymmetry. The values of this function for BeO, BO and CO form a descending series 2.80, 1.94 and 1.43 respectively, whilst for MgO, AlO and SiO the values are in an ascending series 2.06, 2.56 and 2.73 respectively. The change from MgO to SiO therefore appears to constitute an exception to expectation on grounds of symmetry. On the other hand, the electron configuration of SiO is more symmetrical than that of MgO in respect of the electron contributions to the shared group, and this may have something to do with the anomaly, but, if so, increasing symmetry of electron contributions must also be taken into account in the series from BeO to CO. Again, the greater fundamental frequency of CaO as against that of MgO (see section III., case (A)) seems anomalous, but this may be connected with the increase of firmness of binding in the d group of electrons in the Ca atom in preparation for the following transitional element Sc. The effect of inner building in the d group seems clearly shown in the small change of slope from ScO to CrO. Increasing symmetry accounts for the increase in fundamental frequency from CO to NN.

We appear to stand on safer ground in interpreting the descending portions of the curves. The slopes of the NN to ON and NO to OO

is fixed, being O, N or S. The logarithm of the fundamental frequency is shown in relation to the atomic group of X. Let us consider the series from BeO to OO, the maximum lying at CO with its triple bond (see section XI.). There appear to be two oppositely directed influences at work. First, with increasing symmetry of the nuclear masses from

curves are about the same, since in each case we are concerned with the substitution of O for N. On the other hand, the slopes from PO to SO are less, and from NS to SS greater, than from NO to OO. This finds exact correspondence in the relative increases in mass of the atom X in each case: thus S : N = 2.28, O : N = 1.14, and S : P = 1.03 form a descending sequence in the same order.

VI. General Discussion.

It follows from the Rule of Asymmetry (section III.) that the more symmetrical structures tend to be more stable, since a greater fundamental frequency involves greater heat of dissociation (Direction Principle). This also follows from a formula of the pendulum type, since a greater frequency for di-atoms not greatly differing in mass involves a greater elastic force for unit displacement of the nuclei. Nature favours the more symmetrical structures with greater stability, with the consequence that, in a group of orthosteres, the less symmetrical, more polar linkage is less stable than the more symmetrical, more homopolar linkage. Some light is thrown on the transition from polar to homopolar types.

The Rule of Means (section IV.), as applied to internuclear distances, implies that an atom retains more or less constant dimensions in its various possibilities of combination in forming a di-atom. If we consider di-atoms of the type XX, and halve the experimental internuclear distances, estimates may be formed of the working sphere of atoms X, figures which may be compared with the results from crystal data, as in the following table, where the sets of figures from crystal data are mainly as recorded by Sidgwick.³⁰ The agreement is found to be better for homopolar than for metallic linkages. The spectroscopic values for metallic linkages are lower than the crystal values, perhaps due to an absence of "free" electrons in the gas phase.

Di-atom.	$\frac{1}{2}r_e$ (A.U.).		Di-atom.	$\frac{1}{2}r_e$ (A.U.).	
	Spectroscopic.	Crystal.		Spectroscopic.	Crystal.
LiLi	1.34	1.50	FF	(0.67)	0.68
NaNa	1.54	1.84	PP	0.93	0.87
KK	1.96	2.31	SS	0.92	0.92 (S=)
			ClCl	0.99	0.97
CC	0.66	0.67 (C=)	BrBr	1.14	1.13
NN	0.55	0.55 (N≡)	II	1.33	1.35
OO	0.60	0.60 (O=)			

It has been demonstrated that, in crystals, the sizes of certain atoms vary, whether supposed to be associated with single, double or triple bonds. In order to reconcile the spectroscopic and crystal evidence in the above scheme, it is necessary to assume that the bond in CO is double, in agreement with the views of Lessheim and Samuel.²² Evidence derived from the Raman effect,⁴ however, suggested that the link in CO is triple, whilst Hammick, New, Sidgwick and Sutton²⁰ considered that the third link might be semi-polar in character, and the formulation C=O was adopted. The theory of neutralised spins gives a double bond, whilst that of bonding and anti-bonding electrons gives a triple bond. The author⁶ has carefully considered this question, and has

reached the conclusion, based on the group classification, and the same allotted electron configurations to NN and CO, that the link is triple, in the sense that six electrons are mainly concerned in linking the atoms together. However, one pair of these six electrons arise from one atom (oxygen), so that the link is slightly polar, in conformity with an observed small dipole moment. As soon as the three links are formed, there is a redistribution of energy, resulting in a six-electron shared group analogous to that in NN. From another point of view, however, the linkage behaves as if *equivalent in strength to two of the links in NN, with added binding force*, less than that associated with either link, *due to polarity*. The molecule CO may therefore appear to have a double or triple bond depending on the point of view, and this is especially true, since the added polarity is small. The author prefers to say that in CO there is a triple linkage as in NN, with smaller binding force per link as compared with the corresponding link in NN. In the orthostere BF, the linkage will be more polar than that of CO. Evidence derived from bond constants and mean restoring forces calculated by means of a "pendulum" formula gives weight to this view.⁸

The Rule of Periodicity (section V.) turns out to be a wide generalisation, with the general peculiarity that maxima or minima of spectroscopic and bond constants occur in each period in the neighbourhood of the symmetrical sub-group of the tenth group. If ever, therefore, a relation between group number and fundamental frequency can be deduced theoretically, the condition must be satisfied that the function shall have a maximum value for $n = 10$.

It may be observed that Pauling,²⁸ arguing from wave mechanics, suggested that the electronic structure of CO corresponded to a "resonance" mixture of (a) $C \equiv O^+$ and (b) $C = O$. To this assignment, Mulliken²⁶ has added (c) $C^+ - O^-$, with the conclusion that, at the equilibrium nuclear separation, (a) and (c) possess about equal weights. In the views of both the above authors, therefore, a triple bond having polar characteristics is present in CO, in agreement with the above argument, and that from bond constants and mean restoring forces.⁸

Reference may be made to a formula deduced by the author⁴ from relations due to Dadiou and Kohlrausch¹³ of the pendulum type in connection with the Raman Effect. This formula gives:—

$$\omega = C \cdot \sqrt[3]{1/\mu} \quad . \quad . \quad . \quad . \quad (1)$$

where ω is a fundamental frequency for a given linkage, C is a constant for a given type of linkage (2022 for single, 3142 for double, and 4102 for triple bonds), and μ is the "reduced" mass, equal to $MM_1/(M + M_1)$, where M, M_1 are the masses of the nuclei concerned. This relation has been tested for linkages of the three types between pairs of atoms of the K atomic period, and found to be reasonably satisfactory. Some modification would be necessary to adapt it to other periods. The anharmonicity of the vibrations is neglected in deriving the formula.

In conclusion, it may be of interest to trace the history of development of the idea of periodicity in atoms and molecules, which may be destined to have important consequences. First, McLennan, McLay, and Smith²⁴ and Dushman¹⁴ set out the electronic distributions of atoms from atomic number 1 to 92 in periods. Next, the author³ devised a classification in which the atoms (except the rare earths) were arranged in groups as well as periods. The rare earths were afterwards incor-

porated in the scheme.⁵ The significance of this extension seemed to be that atoms of the same group were no longer separated, and it became possible to account for a number of apparent valency anomalies, especially amongst transition elements, in terms of the electron distributions of the atoms concerned. More recently, Grimm^{16, 17} has arranged molecules in a periodic classification, but here the molecules of the same group in different periods which are really members of the same family are separated. The present author has devised the periodic table of molecules, with attention to classification into periods and groups, whereby a number of rules have been discovered, and it becomes possible, for instance, to make predictions concerning certain constants of the halogens and their diatomic compounds thus far not determined experimentally.⁹ The proposed classification throws light on problems of valency and bond strength, and may open up a large field, not only in systematising existing knowledge, but also in indicating lines which future researches may usefully follow. It is hoped that suggestions made in this communication may be found of value in the further study of the spectroscopic and chemical behaviour of di-atoms.

Many indications suggest that the study of di-atoms, and especially those of the type of radicals of short life, may prove useful in clearing up outstanding problems of valency, chemical combination and the mechanism of reaction.

VII. Summary.

A method of classification of non-hydride di-atoms into periods (determined by non-bonding groups of electrons) and into groups and sub-groups (dependent on electrons derived from the incomplete systems of the constituent atoms) has been described. The Convention Principle and the Restriction Principle, explained in the text, are utilised.

Isosteres (or isoelectronic molecules) are sub-divided for di-atoms into three sets, for which the names Orthosteres, Metasteres and Parasteres are proposed. Advantages and applications of this procedure are described.

By means of the Rule of Asymmetry, the Rule of Means, the Rule of Periodicity, and the Direction Principle, which are explained with examples, various regularities and progressions of spectroscopic constants are traced through different groups and periods of di-atoms, and methods of forming estimates of numbers undetermined experimentally are explained. Ways in which the proposed method may throw light on problems of valency and bond strength are also suggested.

A table has been presented showing 1485 di-atoms in their appropriate periods and groups. It is suggested that the properties of these di-atoms, many of which have not been investigated experimentally, may be usefully considered in respect to their positions relative to their neighbours and congeners in the essentially three-dimensional scheme.

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THE STRUCTURE OF THE BENZENE MOLECULE AND SOME OF ITS METHYL DERIVATIVES.

BY PATRICK L. F. JONES.

Received 17th May, 1935.

The object of this work was primarily to prove that in the vapour phase the molecule of benzene and those of its simple methyl compounds are plane, the nucleus having a regular hexagonal structure, and to obtain as accurate values as possible for the interatomic separations in these substances. A considerable diversity of opinion exists as to the carbon-carbon distance in the benzene nucleus. De Laszlo¹ gives 1.41 ± 0.01 Å. from a study of the vapours of the halogen compounds of benzene. Mrs. Lonsdale,² from X-ray studies of crystalline hexamethyl benzene, gives 1.42 ± 0.03 Å. Robertson³ gives 1.41 Å. for crystalline 1, 2, 4, 5-tetra-methyl benzene. Weirl,⁴ from a study of benzene vapour by electron diffraction, gives 1.39 Å. Hendricks,⁵ also by electron diffraction, finds 1.42 Å. for *p*-diiodo benzene vapour. Pierce,⁶ from *p*-di-chlor benzene vapour with X-rays, gives 1.40 Å. Deitz and Andrews⁷ give 1.42 Å. Finally, in a recent paper, Pauling and Brockway⁸ give 1.39 ± 0.005 Å. for benzene vapour.

¹ de Laszlo, *Proc. Roy. Soc.*, 1934, **146A**, 662-700.

² Mrs. Lonsdale, *ibid.*, 1931, **133A**, 536.

³ Robertson, *ibid.*, 1933, **142A**, 659-674.

⁴ Weirl, *Ann. Physik*, 1931, **8**, 559.

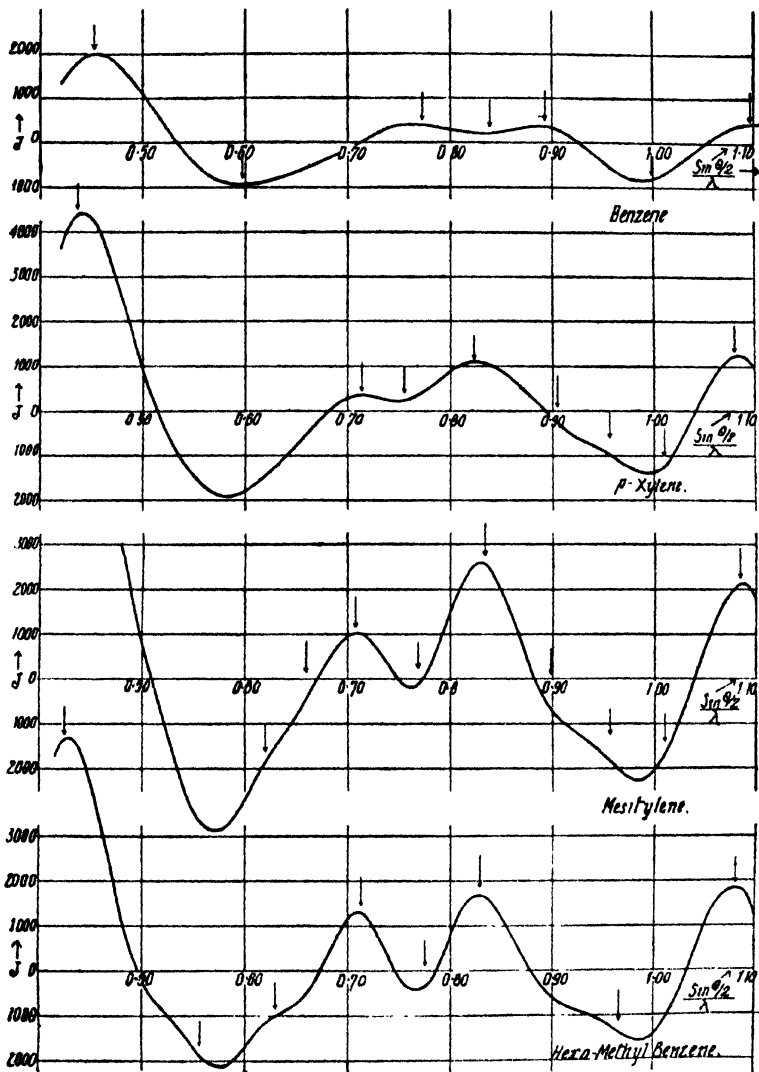
⁵ Hendricks, *J. Chem. Physics*, 1933, **1**, 550.

⁶ Pierce, *ibid.*, 1934, **2**, 1.

⁷ Deitz and Andrews, *ibid.*, 1933, **1**, 62.

⁸ Pauling and Brockway, *ibid.*, 1934, **2**, 873.

It was decided that only substances showing two-fold, four-fold or six-fold symmetry about the centre should be used, so that any possibility of error due to the "ortho effect"^{3, 9} should be eliminated. It is assumed that if the attached atoms are equally spaced round the benzene ring, as is the case in the types of symmetry named, the forces



causing this displacement will neutralise one another. An investigation of hexamethyl benzene vapour was undertaken first, using the apparatus described by de Laszlo,¹ and in the figure are shown the arrows corresponding to the visual maxima and minima. The following values for the $C_{\text{arom.}} - C_{\text{arom.}}$ and $C_{\text{arom.}} - C_{\text{aliph.}}$ distances were tried, with the assumption,

¹ de Laszlo, *Trans. Faraday Soc.*, 1934, **30**, 892.

of a flat regular hexagonal structure in an endeavour to fit a simplified ^{1, 8} Debye scattering curve to these points.

Carom. - Carom.	Carom. - Caliph.
1.41 Å.	1.47 Å.
1.41	1.50
1.41	1.51
1.41	1.53
1.41	1.54
1.41	1.55
1.40	1.50

The last two values given were those used to construct the curve shown and a satisfactory general agreement is found. To check the value 1.40 Å. for Carom. - Carom. it was decided to photograph the vapour of benzene itself, and, on the assumption that this distance retains its value and that the structure is as before, the curve shown (Benzene) was obtained, where the arrows again represent the experimental maxima and minima. In constructing this curve various carbon-hydrogen distances were tried and eventually 1.14 Å. was chosen as the most likely. The correspondence of this curve with the experimental points is good and suggests that the distances used are correct. It must be emphasised that an alteration of ± 0.01 Å. in the values used shifts the maxima and minima appreciably so that the coincidences are upset. This applies equally to the other curves shown.

The values Carom. - Carom. = 1.40 Å. and Carom. - Caliph. = 1.50 Å. were next used for the construction of curves for 1,3,5-tri-methyl benzene and *p*-xylene, and these are shown in the figure. Here again the agreement is good.

In calculating the theoretical curves for these substances, the effect of the hydrogen atoms in the methyl groups has been neglected, firstly because of the uncertainty of the relative orientation of these groups and the possibility of free rotation, and secondly because of the very small degree of scattering they produce owing to the lightness of the hydrogen atoms. The effect of the unreplaced hydrogen atoms in mesitylene and *p*-xylene has been taken into consideration.

The measurements of the ring diameters were made by holding the plate up to a 50-watt electric light bulb with interior etching, and adjusting the distance between the plate and bulb in such a way that the background immediately surrounding the ring under measurement was in each case brought to approximately the same visual density. The diameter was measured by placing a transparent glass scale against the plate parallel to its length. In this way it is also parallel to the axis of rotation of the plate-holder in the camera and any ellipticity due to the plate not having been exactly normal to the electron beam is eliminated.

The justification for the visual method of measurement lies in the remarkable agreement of the $\frac{\sin \theta/2}{\lambda}$ values obtained from the 12 plates taken on each substance at voltages varying from 22 K.V. to 50 K.V., the mean error of the values for any one ring being of the order of 0.2 per cent. for the outer rings ($\frac{\sin \theta/2}{\lambda}$ value greater than 0.6) which are the rings most relied on for the calculation. Pauling and Brockway ⁸ have attempted to give a justification of this method after comparing an extensive series of synthetic scattering photographs with a superimposed background against actual diffraction photographs. They come to the conclusion that the results for the interatomic distances may be relied on to $\pm \frac{1}{2}$ of 1 per cent. We consider, in view of this, and as a result of our work, that the values obtained can be taken as

correct within the limits given and that our assumption as to the structure is justified.

The following Table gives the experimental values of $\frac{\sin \theta/2}{\lambda}$ for the rings used :—

Benzene.		<i>p</i> -Xylene.		Mesitylene.		Hexamethyl Benzene.	
Expt.	Ring	Expt.	Ring.	Expt.	Ring.	Expt.	Ring.
0.357	max.	0.261	max	0.620	max.	0.345	min.
0.453	max.	0.437	max.	0.660	min.	0.424	max.
0.597	min.	0.714	max	0.708	max.	0.557	max
0.773	max.	0.755	min.	0.769	min.	0.629	max.
0.839	min.	0.823	max.	0.834	max.	0.713	max.
0.893	max	0.905	min	0.898	min.	0.775	min
0.999	min.	0.956	max.	0.956	max.	0.829	max.
				1.010	min.	0.966	max
1.097	max.	1.080	max.	1.084	max.	1.081	max.

$C_{\text{arom.}} - C_{\text{atom.}} = 1.40 \pm 0.01 \text{ \AA.}$ } Hexamethyl benzene,
 $C_{\text{arom.}} - C_{\text{aliph.}} = 1.50 \pm 0.01 \text{ \AA.}$ } mesitylene, *p*-xylene.
 $C_{\text{arom.}} - H = 1.14 \pm 0.01 \text{ \AA.}$ } Benzene.
 $C_{\text{arom.}} - C_{\text{arom.}} = 1.40 \pm 0.01 \text{ \AA.}$ }

Summary.

The vapours of hexamethyl benzene, mesitylene, *p*-xylene and benzene have been examined by the electron diffraction method. Theoretical curves constructed, using the interatomic separations given, and assuming a plane molecule with a regular hexagonal structure for the benzene nucleus, have their maxima and minima at points agreeing well with those determined experimentally.

In conclusion I should like to thank Messrs. Imperial Chemical Industries for permission to publish this work, and Professor F. G. Donnan, F.R.S., in whose laboratory it has been carried out. I am indebted also to Dr. H. de Laszlo for help and suggestions.

*The Sir William Ramsay Laboratories
of Inorganic Physical and Chemistry,
University College, London, and
Imperial Chemical Industries Ltd.*

REVIEWS OF BOOKS.

Origins and Development of Applied Chemistry. BY PROFESSOR J. R. PARTINGTON. (London: Longmans, Green & Co. Pp. xii + 597. Price 45s. nett.)

There is much bookmaking nowadays of the Milton's aunt type, much publishing of books about books, of histories that give at third-hand information derived from second-hand sources, and are more concerned with recent developments than with origins. For the history of chemistry

in particular it is a commonplace that Meyer's famous Chapter Five is the one chapter in his classic work which bears evidence of constant thumbing ; and in the matter of origins, for most of us, all is Gas and Geber. Professor Partington has changed all that ; his book breaks new ground, and will inevitably lead to a very different outlook on the part of future historians.

The present reviewer is impelled to say, as the late Mr. Wegg remarked of the Decline and Fall, that he hasn't been not to say right slap through him. Indeed, in discussing a work which involves more than *twenty thousand* separate references to authorities, mostly in the highest ranks, it would be sheer impertinence to attempt a detailed analysis without having the companionship of the book for at least half a year. The utmost he can attempt in a cursory review is to indicate the scope of the work which gathers together the scattered and obscure knowledge of the chemistry and technology of the early civilisations of Egypt, Babylonia, Assyria, Crete, Troy, Cyprus, Persia, Phœnicia and Palestine. In such a study, background is essential, and Professor Partington provides the background for his picture by giving in each instance, a brief outline of the chronology and archaeology of the region, into which the reader may fit the immense variety of facts which the author's scholarship has brought together. His interpretation of the term *Applied Chemistry* is generously wide, and covers such diverse topics as pottery, metallurgy, gems, pigments, glass, textiles, dyes, oils, perfumes, food and medicine.

It would be impossible to make full use of a work of such an encyclopedic character without the assistance of suitable indexes, and it is proper to remark that the book has been most thoroughly and carefully indexed under five separate heads, so that any author, topic or authority can be referred to with the minimum of trouble.

It is not too much to say that the book is destined to give a new impetus to future research on origins, and Professor Partington is to be heartily congratulated on the completion of this portion of what may well prove an unending task.

A. F.

Introducción a la Física Matemática. Volumen II. By ING. ENRIQUE BUTRY, Professor Titular de las Universidades de Buenos Aires y la Plata. Buenos Aires, Imprenta de la Universidad, 1934. 444 pp.

The book under review necessitates a reference to the first volume of the *Introducción* (427 pp.) which appeared in 1931. This formed the eighth of the publications in Serie B of the Faculty of exact, physical and natural Sciences of the University of Buenos Aires, whilst Volume II is Number 11 in this series. The work originated in lectures delivered in 1927-1930 and is based on notes taken by students, three of whom are specially mentioned. The author states in the preface that he considers it better to treat the subject from the standpoint of mathematical theory rather than start with several chapters on mathematical physics, and this course has been followed throughout the work.

The treatment is largely from the point of view of the vectorial calculus which the author uses not merely on account of its simplicity, but also for the direct and intuitive form which it gives to geometrical and physical quantities. The Cartesian representation is also introduced but occupies a subordinate place. To read the book intelligently, a certain mathe-

mathematical equipment is necessary, viz.—a knowledge of complex quantities, determinants, the analytical representation of curves and surfaces and the differential and integral calculus.

The work starts with the definition of scalars and vectors, explains the notation adopted and proceeds to the consideration of scalar, vector and mixed products. In dealing with the rotation of vectors, ϵ is introduced as an operator and subsequently identified with $\sqrt{-1}$. The second part of the first volume (*Cálculo Tensorial*) is divided into three chapters which deal respectively with Tensorial Algebra, Tensorial Analysis and Vector Fields. Certain paragraphs dealing with a multiplicity of dimensions are marked with an asterisk; they are arranged in logical sequence, and the reader may please himself as to confining himself to three dimensions. The second and third chapters are noteworthy for the concise manner in which the differential operators and the theorems of Gauss, Green and Stokes are dealt with. The third part is principally concerned with tensors of the second rank and the first volume concludes with useful appendices dealing, amongst other matters, with determinants, matrices, change of variables, surface integrals to line integrals, volume integrals to surface integrals.

The second volume is divided into two parts, these are entitled *Elementos de Geometría Diferencial* and *Cálculo Tensorial (Para Transformaciones afines y continuas)* respectively. The author starts with the representation of a curve by the continuous function $P = P(t)$ and deals rapidly with the representation of tangent, normal, binormal and the osculating, normal and rectifying planes. First and second curvatures and the centre of curvature are also dealt with, Chapter II being more especially devoted to contacts and osculation and Chapter III to the development of surfaces, involutes and evolutes.

Chapter IV is entitled *Superficies* and introduces Gaussian co-ordinates; in dealing with elements of area the author refers to works on analysis for more rigorous demonstration but a clear idea may be gained as to the coefficients $g_{\mu\nu}$ and the associated coefficients $g^{\mu\nu}$ and the symmetry of the Christoffel symbols

$$\left[\begin{smallmatrix} \mu\nu \\ \sigma \end{smallmatrix} \right] = \left[\begin{smallmatrix} \nu\mu \\ \sigma \end{smallmatrix} \right],$$

with respect to the upper indexes. Curvature and geodesics follow and the chapter concludes with a small paragraph on the conception of parallel displacements.

The second part of the volume consists of four chapters entitled respectively *Cálculo Tensorial*, *Espacios Riemannianos y Pseudoriemannianos*, *Cálculo Diferencial Absoluto* and *Aplicaciones Geométricas—Curvatura*; this gives a fair idea of the material treated therein. A list of works consulted by the author, corrections of misprints and table of contents complete the book.

The notation adopted is understandable, vectors are printed in bold-faced type and it may be mentioned that the signs ∇ and ∇^2 are used for *nabla* and the Laplacian operator respectively. The signs for scalar and vector products are not usual in this country.

Both printing and general appearance of the work are excellent and the diagrams, though not numerous, are adequate and plain. Since the re-

viewer is neither a mathematician nor a physicist, and possesses but a rudimentary knowledge of Spanish, he feels diffident in passing an opinion on the work. The conclusion arrived at is that the author has achieved his aim and produced a book which for logical arrangement and clearness of expression is of outstanding merit.

If an outsider is permitted an opinion on mathematical symbols, may he express the hope that an agreement may be come to regarding the signs used for scalar and vectorial multiplication. Chemists may be indifferent as to whether they call a certain compound prussic acid, formonitrile, Blausäure or acide cyanhydrique, but all agree as to one symbol, HCN.

An Introduction to Atomic Physics. By JOHN THOMSON. (London: Methuen & Co., Ltd. Pp. vi + 223, with 4 plates and 36 diagrams. 1935. Price 10s. 6d. nett.)

Dr. Thomson's book contains a very lucid and careful treatment of the fundamentals of atomic physics, which may be read with profit by a student entering upon an honours course of lectures. It is divided into three main sections. Part I deals with the experimental basis of atomic physics, Part II with the theory of atomic structure, and Part III with molecular, atomic and nuclear radiations. Good accounts are given of the Bohr atom, of the Hamiltonian wave-mechanics, and of wave-mechanics as developed by Schrödinger and de Broglie. The hydrogenic atom is considered in some detail. The mathematics involved is not too heavy, and physical principles are kept well to the fore. If a very minor criticism may be ventured, it is that accounts of experimental work might be more full. After all, atomic physics has its roots in experiment. The book may be strongly recommended.

A. F.

Physics for College Students. By Professor A. A. KNOWLTON. (London: McGraw Hill Publishing Co., Ltd. 1935. (Second Edition.) Price 21s. nett.)

Professor Knowlton's book represents the endeavour of a successful teacher of original mind to answer the question, *Why study physics apart from its technical and technological values?* And it may at once be said that the book provides a very complete justification of Physics as a cultural subject. The disjointed treatment of the ordinary text-book disappears and the subject is developed with the doctrine of energy as the central theme. The fifty-seven chapters of the book, beginning with "Measuring the work which a machine does" and ending with "The production of radiation" and "The structure of atoms" lead the student to the confines of existing knowledge without omitting any important topic by the way. The treatment is elementary throughout, and a most valuable, and indeed essential, feature of the book is provided by the carefully graded quantitative problems and topics for discussion which are appended to each chapter.

A. F.

Errata. *This vol.*, p. 825, 15th line from top, for "qualitatively" read "quantitatively".

A GENERAL DISCUSSION ON "THE STRUCTURE OF METALLIC COATINGS, FILMS AND SURFACES."

Friday and Saturday, 29th and 30th March, 1935.

THE SIXTY-SECOND GENERAL DISCUSSION OF THE FARADAY SOCIETY was held at The Imperial College of Science and Technology, London, S.W. 7 by kind permission of the Rector on the 29th and 30th March, 1935.

The meeting was held in the Metallurgy Theatre, the President, Mr. William Rintoul, occupying the Chair. By the courtesy of the Rector, the Imperial College Union was open for the convenience of those attending the meeting, and the Guest Night Dinner was held there to honour the overseas guests of the Society. There were no formal speeches, but the toast of the overseas guests was proposed by the President and a reply was given by Professor Schlötter. On the evening before the meeting the Society's guests attended the Anniversary Dinner of the Chemical Society at Grosvenor House, and after the Guest Night Dinner on Friday evening, they were present at the Friday Evening Discourse at the Royal Institution, given by Lord Rutherford of Nelson on "The Neutron."

At the inaugural meeting the President introduced the overseas members and visitors attending the meeting, and in accordance with the usual custom of the society, these ladies and gentlemen were called upon to rise in their places so that they might be welcomed with acclamation by the Society. Amongst those so welcomed were: Dr. and Mrs. W. Blum (*Washington*), Professor A. Glazunov (*Přibram*), Professor V. Kohlschutter (*Bern*), Dr. E. Liebreich (*Berlin-Halensee*), Professor L. S. Ornstein (*Utrecht*), Professor H. H. Paine (*Johannesburg*), Dr. H. Reininger (*Leipzig*), Professor M. Schlötter (*Berlin*), Professor J. J. Trillat (*Besançon*), and Professor L. Tronstad (*Trondheim*).

The Secretary read letters and telegrams from the following guests who had unavoidably been prevented from attending: Professor H. G. Grimm (the President of the Deutsche Bunsen-Gesellschaft), Professor F. Kirchner (*Leipzig*), Mr. D. J. Macnaughtan (who was still in America), Dr. E. Müller (*Dresden*) and Professor A. Portevin (*Paris*).

The General Introductory Paper was given by Professor C. H. Desch, after which the various papers, which had been circulated in advance, were discussed.

The papers were taken as read and discussed under two broad heads:—

Part I.—Electron Diffraction Methods.**Part II.—The Structure of Metallic Coatings.**

At the conclusion of the meeting a brief summarising statement was made by Professor G. I. Finch, and Professor Desch indicated that he would summarise the discussion in writing.

The meeting concluded with votes of thanks to the overseas guests for their presence and assistance in assuring its success, to which Professor Schlötter replied; to the Rector, Professor Sir C. H. C. Carpenter and Professor G. P. Thomson for the hospitality accorded to the Society and to the laboratory staff for all their assistance in securing the success of the meeting. Votes of thanks were also accorded to the members of the organising committee, namely, Professor C. H. Desch (Chairman), Dr. N. K. Adam, Dr. H. J. T. Ellingham, Professor G. I. Finch and Mr. D. J. Macnaughtan, and also to the translators of papers. The meeting concluded with a vote of thanks to the President and the Society on behalf of the overseas guests, which was proposed by Professor Schlötter.

The Reports and the Discussion thereon and Summary appear in the following pages.

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THE STRUCTURE OF METALLIC COATINGS, FILMS AND SURFACES.

INTRODUCTORY PAPER.

BY CECIL H. DESCH, D.Sc., F.R.S.

Received 19th March, 1935.

When we consider how much of our immediate knowledge of metals is derived from their surfaces, it is rather surprising to find how scanty is our information as to the true properties of the surface of a metal. This comes from the fact that the outer layer of a solid is chemically unsaturated, so that it can attach to itself foreign ions, atoms or molecules, forming a film, often monatomic, which covers the true surface. The unsaturation results from the unsymmetrical nature of the forces at the surface, in contrast with the symmetrical attractions in the interior of the mass. The surface of a metal, unless prepared by evaporation or sputtering in a high vacuum, is normally covered by an adsorbed layer of gas, which on many metals soon assumes the form of a thin layer of oxide, hydroxide, or other compound.

We are chiefly concerned in the present discussion with surfaces which have been so exposed, the properties of which may be, and frequently are, quite different from those of an uncontaminated surface. When attempts have been made, for instance, to determine the angle of contact between a liquid and a solid, the results have almost always been vitiated by the presence of an adsorbed film, which prevents the two substances from ever coming into direct contact. This is illustrated by the behaviour of two non-metallic materials, glass and quartz. Schumacher¹ found that the angle of contact with mercury changed as cleaning of the surfaces was carried further, and it appeared that if the film could be completely removed both solids would be wetted by mercury. The present discussion is not concerned with the mechanism of adsorption on solids, which was dealt with in a previous symposium,² but the influence of the film on metals which have been exposed to air will be discussed. Thicker films, approaching scales, such as are produced at high temperatures, will not be considered.

The study of surfaces has been immensely facilitated by the introduction of the method of electron beam diffraction, which we owe mainly to Professor G. P. Thomson, and for this reason the first part of the discussion is entirely devoted to that subject. Whilst X-rays penetrate so deeply as to reveal the structure of the underlying solid and to miss that of the surface film, when excessively thin, the low penetration of the electron beam offers a great advantage, and it is by the use of this important research tool that the greatest progress in this field has been made. We are fortunate in having contributions on this subject from the pioneers in the use of diffracted electron beams, and the triumphant success of the method in its application to surfaces is being shown to us.

¹ E. E. Schumacher, *J. Amer. Chem. Soc.*, 1923, **45**, 2255.

² *Trans. Faraday Soc.*, 1932, **28**, 139 ff.

One of the most interesting questions concerning metallic surfaces, which it has been possible to answer as the result of applying the new method, is that of the nature of the layer produced in polishing. Grinding with an abrasive, as was shown 270 years ago by Robert Hooke,³ merely results in the formation of grooves, which become finer and finer as the grain size of the abrasive is reduced. Rayleigh⁴ showed that in the polishing of glass the process was quite different, and that irregularities were smoothed out rather than ploughed away. Beilby, in a series of papers from 1903 onwards,⁵ observing the process of polishing, both on metals and on non-metallic solids, came to the conclusion that the action of the polishing process was to cause the surface layer to flow like a liquid, this flowed layer then rapidly congealing without crystallising, so that the surface of a polished substance was covered by a thin layer of an amorphous or, as he preferred to call it, "vitreous" modification, chemically identical with the underlying solid, but devoid of crystal structure. The evidence for this view was provided by a very beautiful series of experiments of extreme simplicity, an account of which was subsequently collected in book form.⁶

The hypothesis of the "Beilby layer" was much debated among metallurgists, the non-metallic aspect of the question receiving less attention. Objections were raised on the ground that the production of a vitreous phase, which might be regarded as an undercooled liquid, could not be reached by mechanical means in a range of temperature within which only the crystalline phase was stable. On the other hand, it was argued that the flowed layer was not produced by hydrostatic pressure—a fact proved by experiment—and that under shearing stress such a transformation was possible. The writer has reviewed the evidence elsewhere.⁷ The matter was complicated by the use of the hypothesis to explain the work-hardening and fatigue of metals, and also by the extension of the conception of an amorphous film to an inter-crystalline layer in cast metals. This last development, although suggested several times by other investigators, was mainly due to Rosenhain, and formed no part of Beilby's original hypothesis. It is not supported by modern theory. In the controversies which ensued the character of the superficial polished layer was rather neglected, the application to cold-working receiving most attention. Continental metallurgists never accepted it, and in recent years the tendency has been for the idea to be neglected in favour of the rival view, that the polished layer consists merely of crystals broken into fragments and perhaps more or less orientated. There is naturally a point at which the two hypotheses become indistinguishable, when the crystal size falls below that necessary to produce a pattern with X-rays, and as time went on the distinction became somewhat artificial. It may be said that the evidence of the electron beam method is conclusive, and the present papers by Professor Finch and his collaborators and by Mr. Hopkins seem to place the matter beyond doubt. It is a matter of great regret that Sir George Beilby, who was keenly interested in the work of the Faraday Society, did not live to see his experimental work vindicated by evidence of an entirely

³ "Micrographia," 1665, Observation II.

⁴ Lord Rayleigh, *Proc. Roy. Inst.*, 1901, **16**, 563.

⁵ G. T. Beilby, *Proc. Roy. Soc.*, 1903, **72**, 218, 226; *Phil. Mag.*, 1904, (vi.), **8**, 258; *J. Soc. Chem. Ind.*, 1903, **22**, 1166.

⁶ "Aggregation and Flow of Solids," 1921.

⁷ "The Chemistry of Solids," Oxford Univ. Press, 1934.

new kind. It may now be accepted as a fact that the surface of a polished metal is of such a fine structure as to be incapable of giving a crystalline pattern with electron beams. That, like a liquid, it has the power of rapidly dissolving atoms of a foreign metal, has been shown by Professor Finch. That Mr. Lees has found the layer on his copper specimens to consist of cuprous oxide is perhaps accounted for by his use of an electrolyte capable of producing a passive layer in the course of removing the surface film. Mr. Hopkins's method of sputtering would not give rise to oxidation.

That an oxidisable metal, such as iron, copper, or aluminium, quickly becomes coated in air, in the case of copper with gentle warming, with an invisible film of oxide, has proved to be highly significant for the problem of atmospheric corrosion. Even at a thickness which is below that required to produce interference colours, such a film is highly protective, and it has been shown that the resistant quality of "stainless" steel is due simply to the presence of a self-healing film of oxide of iron and chromium.⁸ Aluminium, deposited on glass by evaporation *in vacuo*, covers itself with a film so thin as not to interfere with its use for astronomical mirrors, and yet extremely resistant to further oxidation.⁹ The nature of these films is discussed in some of the contributions to this Discussion, and the mechanism of their formation is under examination at the National Physical Laboratory in connection with their permeability to gases.¹⁰

Other papers before us deal with the more abstruse question of the physics of electron diffraction, and afford an opportunity of clarifying our ideas on this subject.

Turning now to the production of protective coatings on metals, the application of entirely foreign materials, such as paints and lacquers, is excluded from the Discussion, and electro-deposited coatings receive the greatest amount of attention, although we also have contributions dealing with hot-dipping and with spraying. Electro-plating has too long been a merely empirical art, and the interest shown in several countries in recent years in the principles underlying its practice is a healthy sign. In this connection the formation of the Electroplaters' and Depositors' Society, in close association with the Faraday Society, of which it may be regarded as an offshoot, has been of great benefit to the industry in this country.

Several of the communications deal with the relation between the hardness of electrolytic deposits and the conditions under which they have been deposited. Hardness, as shown in the paper by Mr. Wood, may be caused either by minute grain size or by lattice distortion, and he indicates means of distinguishing the two cases. A comparison with the other papers which describe the properties of electro-deposited nickel shows that microscopical examination does not, for that metal, suggest a grain size which is small enough to account for the observed effect, and the question arises, and will doubtless be discussed, whether the grain size measured by the X-ray method is identical with that determined microscopically, or whether it corresponds rather with an internal mosaic structure of smaller dimensions. The work of the Research Department at Woolwich has shown that the precipitation of nickel hydroxide together with the deposited nickel is largely responsible for

⁸ U. R. Evans, *J. Chem. Soc.*, 1927, 1020.

⁹ H. Spencer Jones, *Nature*, 1934, 134, 522 (Oct. 6).

¹⁰ G. D. Preston and L. L. Bircumshaw, *Phil. Mag.*, 1935 (vii.), 19, 160.

increased hardness, and that the changes in the nature of the deposit with changing acidity of the solution are largely due to such precipitation. Internal stress in the deposits is affected by the same cause, and it was shown in the writer's laboratory at Sheffield that the stress in nickel varied directly as the deposition potential, so that by superposing alternating on direct current, and thus preventing the deposition potential from building up to its normal value, deposits almost free from internal stress could be obtained.¹¹ Light is thrown on the mechanism of this co-precipitation by the papers contributed by Dr. Liebreich, Dr. Müller, and Professor Kohlschütter, whilst other papers on electro-deposition deal with closely related subjects. Dr. Blum, to whom much of the increased attention given to the process of electroplating owes its origin, contributes a paper on nickel deposition at high current densities.

The fact, shown by Mr. Macnaughtan, that nickel oxide migrates in electrolytic nickel on annealing,¹² is one of particular interest, and suggests that fine dispersion of non-metallic matter through the crystals may be partly responsible for hardness, by a mechanism similar to that of the age-hardening of alloys. The extreme hardness of electrolytic chromium, which is one of its principal practical advantages, calls for explanation, and the papers before us provide ample material for its discussion. Professor Portevin and also Mr. Hotherhall deal with the influence of the basis metal on the structure of deposits, and it is interesting to see how the deposit will continue the crystal form of the underlying metal, even when there is a considerable difference in lattice constants. This recalls the work of Professor Finch, in which one metal was deposited in an exceedingly thin film on another, but in electro-deposition the effect appears to extend over a great thickness of deposit. For a complete understanding of the process of growth of electrolytic deposits it is evidently necessary to take into account the structure of the two lattices, and ultimately also the residual attractions acting at the surface. The problem thus reduces itself largely to a question of physics. This is true even of the relatively simple process of hot-dipping, dealt with by Mr. Daniels. The efficiency of the tinning and similar processes depends on the wetting of the basis metal by the liquid metal, and wetting is itself a manifestation of the residual surface forces. There is thus a theoretical link, as well as a merely practical one, between the subjects dealt with by our contributors. It has not been possible to mention all the papers submitted, some of which have not been seen, but the present seems an exceptional opportunity of comparing the conclusions of a number of workers, both on the theoretical and on the practical side, on problems which find their common object in the study of metallic surfaces, the scientific examination of which has been so greatly facilitated by the introduction of new experimental methods.

¹¹ R. H. D. Barklie and H. J. Davies, *Proc. Inst. Mech. Eng.*, 1930, 731.

¹² G. E. Gardam and D. J. Macnaughtan, *Trans. Faraday Soc.*, 1933, **29**, 755.

PART I. ELECTRON DIFFRACTION METHODS.

AN APPARATUS FOR ELECTRON DIFFRACTION AT HIGH VOLTAGES.

BY PROFESSOR G. P. THOMSON, F.R.S.

Received 5th February, 1935.

The ordinary gaseous discharge tends to become unsteady at voltages exceeding about 45,000 and if it is desired to work with electrons of greater energy than this, some modification of the normal type of electron camera is desirable. Two possibilities present themselves, one the use of a hot cathode discharge, the other the method of two-stage acceleration which has been much used for positive ions. I decided on the second method for the following reasons: firstly, it avoids most of the X-rays which at high voltages would require rather elaborate shielding, secondly, it yields monochromatic electrons without the use of very large condensers, or subsidiary devices such as deflecting magnetic fields which would be difficult to combine with the existing apparatus.

Mechanical Arrangement.

The arrangement to be described has, in fact, been fitted to an existing apparatus of the Thomson-Fraser type without altering the crystal chamber or plate-carrier. Fig. 1 shows the set-up. The glass discharge tube A is fitted on to the copper base B by a ground joint sealed with Apiezon Q compound. The joint is air-cooled, using copper fins, the circulation being assisted by a fan a few feet away. The anode C is a copper rod with a conical end pierced at the tip with a hole 0.2 mm. diameter, communicating with one of 9 mm. through which the electrons pass into the copper tube D. A tube E leads air from a capillary leak into A from which it is drawn again through the tube F by a Hyvac pump. This pump is insulated on vulcanised pillars and driven by a leather belt from a motor 50 cm. away. A discharge takes place in A at a pressure which can be altered, if required, either by changing the capillary or by throttling the pump by means of a tap. In practice, alteration is seldom necessary, and the capillary once adjusted, does not need attention.

The cathode rays from the discharge in A are accelerated by the field applied between the polished copper tubes D and G which are rounded at the ends with copper stress distributors. The rays then pass through a second fine hole, also of 0.2 mm. diameter in an aluminium disc at H and so enter the crystal chamber where they are diffracted by the specimen

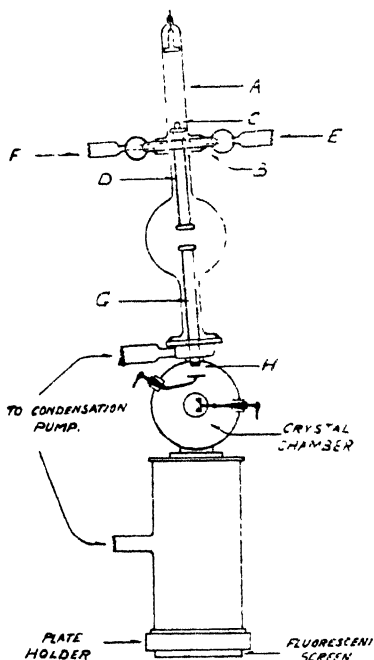


FIG 1.

in the ordinary way and eventually reach the fluorescent screen or photographic plate. The crystal chamber and camera are earthed.

Electrical Lay-out.

An induction coil rectified by a valve supplies the current for the discharge in A, the intensity of which can be regulated by means of the valve.

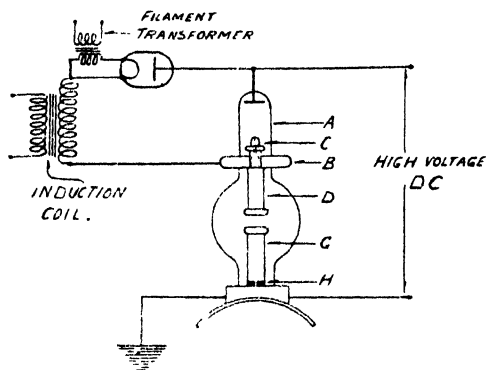


FIG 2

The main high tension voltage is applied between the cathode of A and earth (see Fig. 2). A set using the Cockcroft doubling principle and generating up to 160 K.V. being available, is used for the purpose, but the full voltage has never been required. The high tension condensers have a capacity of 0.02 microfarads, the frequency is 50 cycles. As the only current necessarily taken from this circuit is that in the cathode rays which enter the fine hole in C a very high degree of constancy of voltage is attained. A milliammeter in

the H.T. circuit reads about 0.1 milliamp., mostly due to brush discharge and a faint discharge in the tube connecting A with the Hyvac pump.

Results.

The apparatus as described works well over a range of voltage of 45-85 K.V. the upper limit being at present imposed by the insulation of the filament transformer of the valve for the discharge in A. The rest of the insulation will stand 100 K.V. A pattern taken at 83 K.V. is reproduced in Fig. 1*. The spot becomes rather faint below about 45 K.V. owing to the long distance between the fine holes limiting the beam.

Electrostatic Focusing.

Interesting effects can be observed by varying the voltages on the two stages. Owing to the shape of the field between D and G there is a strong electrostatic focusing of the rays, and it is possible, by adjusting the fields, to take photographs showing sharp patterns with the lower diaphragm removed, the rays from the fine hole in C being focused directly on the plate. In the circumstances, the spot is extremely bright and it is difficult not to overexpose the plate using the ordinary hand shutter. Since, however, the focussing depends on the constancy of the two discharge potentials it is doubtful if it is a very practical method of working. In addition, in the apparatus as at present set up, there is a good deal of diffuse illumination on the screen due to electrons scattered at the inside of the tubes D and G; this could be reduced by increasing the diameter of these tubes. A very bright spot, but an ill-defined one, is seen if the voltages are such as to form an image of the hole in C near the hole in the lower diaphragm, thus effectively reducing the distance between the holes on which the definition depends. This arrangement might be useful if it were necessary to look for faint

* Plate I.

diffraction patterns on the fluorescent screen, when a suitable specimen was found the voltage could be altered to give a sharp spot and a photograph taken.

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ELECTRON DIFFRACTION AND SURFACE STRUCTURE.

BY G. I. FINCH, A. G. QUARRELL AND H. WILMAN.

In 1927 G. P. Thomson¹ showed that electrons could be diffracted. In doing so, not only did he put de Broglie's wave-theory of matter on an experimental basis, but he also foresaw the potentialities of electron diffraction as a means of studying surface structure problems.² It is the object of this communication to outline the present state of the technique of electron diffraction and to illustrate, by examples drawn principally from the study of metallic films and surfaces, some directions in which the new method is being applied. (See Plates II to XXVIII.)

The Technique of Electron Diffraction.

An electron diffraction camera consists of a device for producing a fine beam of electrons moving at a controlled velocity, an arrangement for holding the specimen to be examined in any desired position relative to the beam, and visual and photographic means for observing and recording the angular distribution of the diffracted electrons.

Two types of diffraction camera are in use in this laboratory. In the first the highest degree of precision is aimed at; the second is used for that large class of problems which may be solved by a determination of the lattice constants to within 2 per cent., or by the detection of a change in crystal structure, or even by determining whether a given specimen is crystalline or not. In both types the design aims at maximum pattern definition and clarity, beam intensity, reliability, convenience, economy and speed in operation, combined with ease of construction.

Precision Electron-Diffraction Camera (Fig. 1).

Cathode Chamber Assembly.—The glass cathode chamber consists of a straight-necked wine bottle from which the base has been cut off and the neck and body apertures ground normal to the axis. It is sealed with picein wax into a groove in a brass block, the lower surface of which is ground with coarse carborundum paste on a surface plate and suitably greased to make a vacuum-tight joint with the brass anode block. Internal flanges protect the picein and grease from bombardment by the discharge which would otherwise result in irregular gas evolution. A highly polished massive aluminium rod screwed into a brass block serves as cathode, a vacuum-tight joint being made with the neck of the bottle by means of a rubber washer. Since this joint is easily made and broken, it is a simple matter to withdraw the cathode for repolishing and to remove sputtered metal from the walls of the discharge vessel. In practice, this is important because pitting of the cathode surface in time affects the steadiness, homogeneity and cross-sectional area of the electron beam. An excessive deposit of sputtered metal on the walls of the discharge tube exerts a similar effect and may also lead to puncturing of the glass.

Collimating Section.—The beam is collimated by a single diaphragm in the water-cooled anode block followed by magnetic concentration.

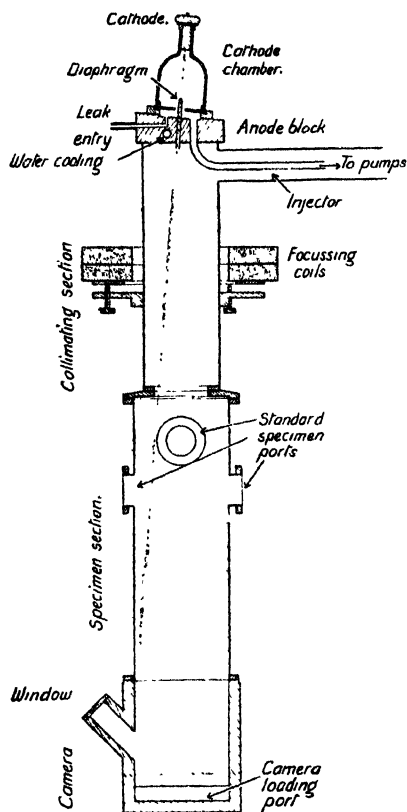


FIG. 1.—Precision Electron Diffraction Camera.

motions are obtained will be evident from the figure. The several types of specimen holders, each suited to a particular form of specimen, are interchangeable and screw into the end of the main stem of the specimen carrier.

The Camera or Recording Section.

The camera consists essentially of a hollow cubical bronze casting. The upper face carries a circular flange which is ground to make a vacuum-tight joint with the specimen chamber. An observation tube cast on one of the sides of the cube is so arranged that every part of the fluorescent screen is visible, the end of the tube being ground and closed with a plate glass disc. At the bottom of an adjacent side is a rectangular slot, the

An important feature of the anode block is that its upper surface is so inclined to the main axis of the apparatus that the axis of the discharge tube passes to one side of the fluorescent screen. The diaphragm is a 4 mm. internal bore brass tube, spun over and drilled out at the upper end to 0.1 mm. diameter. The two independent focussing coils consisting of about 1500 ampère-turns are adjustable in height and tilt about the axis of the instrument.

The Specimen Chamber.

The specimen chamber contains four 2-inch internal diameter ports, one pair near the upper end of the tube and the other a short distance below. Each port is fitted with a standard ground surface so that the specimen carrier may be used in any one of the four ports. The normal effective camera length (50 cm.) can be approximately halved by inverting the specimen chamber. The specimen carrier is shown in detail in Fig. 2. The necessary independent motions of the specimen are as follows: (i) inclination of the plane of the specimen to the electron beam, (ii) translation into the beam, (iii) rotation in the azimuthal plane, and (iv) lateral motion in the specimen plane at right angles to the electron beam. The manner in which these

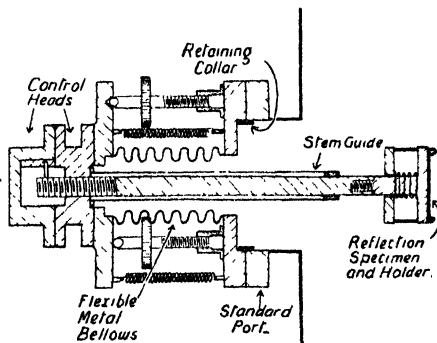


FIG. 2.—Specimen Carrier.

camera loading port, surrounded by a raised ground surface and closed by a ground brass plate, a vacuum-tight joint being made by means of a degassed rubber gasket.

The brass plate, *P*, carries the plate holder and shutter mechanism and is shown in plan and elevation in Figs. 3a and b respectively. The photographic plate is held in a recess in the brass frame, *K*, and immediately above it is the shutter which rotates about the axis, *OO'*. The shutter is divided into two halves, *A* and *B*, which are mounted on concentric hollow axes, *C* and *D*, respectively, with bearings at each end. The axle *C* is continued through the brass plate, *P*, and fitted with a control head, *E*; the other axle passes through both *C* and *E* and is fitted with a second control head, *F*. A fluorescent screen completely covering both half-shutters is attached to two short collars, *G*, which can rotate freely about the axis *OO'*. Rotation through 90° of either head *E* or *F* raises the half-shutter *A* or *B* respectively, together with the loosely hinged fluorescent screen, thus exposing the corresponding half of the photographic plate.⁸ When required, the two shutter halves can be raised and lowered together. The heads *E* and *F* are suitably ground and lubricated to make vacuum-tight joints.

Vacuum Technique.—The diffraction camera is evacuated by means of a four-stage mercury vapour diffusion pump backed by a small rotary oil pump. Short wide-bore connections are used, and ingress of mercury vapour into the apparatus is effectively prevented by an injector system in which a stream of gas from the cathode chamber drives back mercury vapour diffusing over from the pump.⁶ The pressure within the cathode chamber is controlled by means of a leak system consisting of a length of $\frac{1}{32}$ -inch bore copper tubing connected with a gas reservoir in which the pressure can be adjusted to any desired value. A suitable leakage resistance is obtained by flattening the tube to a greater or lesser extent with pliers. The vacuum-tightness of the camera depends in the main upon that of a number of ground metal joints lubricated with a grease made by digesting 2 per cent. of crêpe rubber in pure white petroleum jelly *in vacuo* on a boiling brine bath. Permanent joints are soldered, and semi-permanent joints are made with picein wax. The pressures within the discharge chamber and specimen section can be measured with

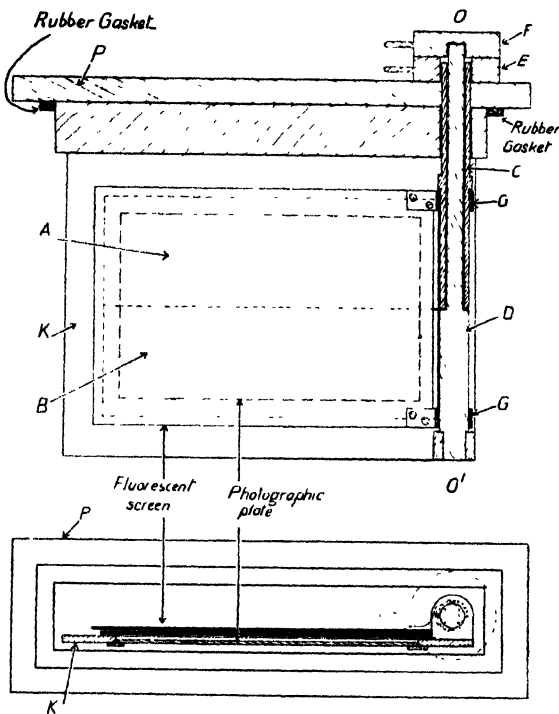


FIG. 3a.—Plan.

FIG. 3b.—Elevation.

FIG. 3a and 3b.—Shutter Mechanism.

Pirani and ionisation gauges respectively, or by means of suitable McLeod gauges; but such methods of measurement are not advocated because the spark gap between 10 cm. diameter spheres in parallel with the discharge chamber forms an efficient and far more convenient substitute. Thus, if no discharge passes in the cathode chamber at 100 KV. when the leak supply to the cathode chamber is cut off, then vacuum conditions in the diffraction section will be satisfactory. During pumping down, the progress of evacuation can be easily followed; at first by the appearance of the discharge, and then by the voltage as measured by the sphere-gap voltmeter.

High Tension Supply.—The circuit of the constant current high-tension supply system is shown in Fig. 4. The reactance of the 50 ~, 220V./120KV. transformer is increased to about 30 per cent. by a choke

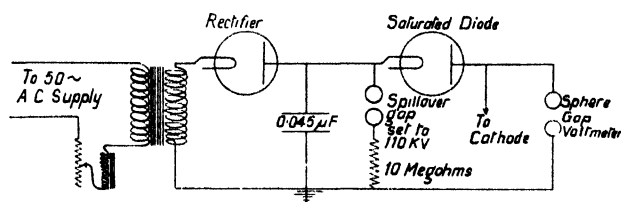


FIG. 4.—High Tension Supply.

by a 220 KV. diode to fill a 0.045 μ F. Ferranti condenser protected by a spill-over gap set to 110 KV. Current flows to the cathode of the discharge tube through a 120 KV. diode which is run under conditions of saturation, the filament temperature and therefore the high-tension current passed being under exact control. The output of this equipment is sufficient to supply four diffraction cameras simultaneously, provided each is fed through a separate saturated diode.

The range over which the cold cathode tube can be used is between approximately 15 and 80 KV. Below 15 KV. the electron beam contains too large a proportion of electrons which have lost energy through collision with gas molecules in the discharge chamber; on the other hand, it is difficult to obtain steady discharge conditions with pressures exceeding about 80 KV. It so happens, however, that the most useful range of accelerating voltages for structure analysis lies between about 30 and 70 KV. Under these conditions a cold cathode source is to be preferred to a thermionic emitter, not only for reasons of robustness and simplicity, but also because use can be made of its peculiar properties in order to obtain a monochromatic electron beam. Of the three discharge conditions in the cold cathode tube, namely gas pressure, current and voltage, the fixing of any two determines the other. The pressure is readily controlled by means of the cathode chamber leak and, provided the voltage across the condenser never falls to a value less than the sum of the cathode potential fall and the saturation voltage of the current-controlling diode, a supply of constant current to the cathode is easily ensured. Thus a constant accelerating voltage can be obtained with relatively simple equipment.*

No matter whether a hot or a cold cathode tube is used, the beam passing through the anode diaphragm contains unwanted, indeed harmful, components. In the cold cathode tube these consist of molecular rays and electrons which have lost energy by elastic collisions, while with a hot cathode the beam will include molecular and light rays. By tilting the axis of the discharge chamber, however, the electron beam and its unwanted components can be trapped. If the concentrating field is suitably adjusted and biased, the molecular and light rays remain trapped, but the electrons, including those which have lost energy by collision, will be released, to pass into the specimen chamber in the form of a magnetic

in the primary circuit and is sufficient to afford ample protection to the secondary. One end of the secondary is earthed, and the output is half-wave rectified

spectrum in which most of the energy is concentrated in that part which corresponds to electrons which have lost no energy. A diaphragm mounted on a second specimen carrier immediately above the specimen enables the slower electrons of the spectrum to be filtered out, thus ensuring that the diffracted electrons have energy and therefore wave-length corresponding to the accelerating voltage.

A single diaphragm followed by magnetic concentration is a much more efficient method of collimation than a double or tubular diaphragm; but, if distortion of the diffraction patterns is to be avoided, it is essential that wherever the concentrating field extends beyond the specimen it shall be uniform in planes at right-angles to the beam axis up to the limits of their intersections with the cones or rays of diffracted electrons.¹¹

Small Camera (Fig. 5).

The essential features are similar to those in the instrument described above, the main difference being in the design of the recording section and of the specimen carrier. Owing to the reduced size of the camera, it is convenient to construct the collimating section, specimen chamber and recording section as a single unit supported on a suitable stand. The specimen carrier is shown in detail in Fig. 6. It will be seen that translation into the beam and rotation in the azimuthal plane are independently obtained through a single ground joint, *J*, the rotatable control head, *H*, of which carries a stout rod, *T*, threaded into the main stem, *S*, of the carrier. Turning the control head rotates the main stem without translation until the blade, *L*, comes into contact with the rod, *R*, whereupon the motion is changed to translation without rotation. The camera, consisting of a circular brass block in which is machined a recess for the photographic plate, is placed into position from below, a vacuum-tight joint being made by means of a rubber gasket.

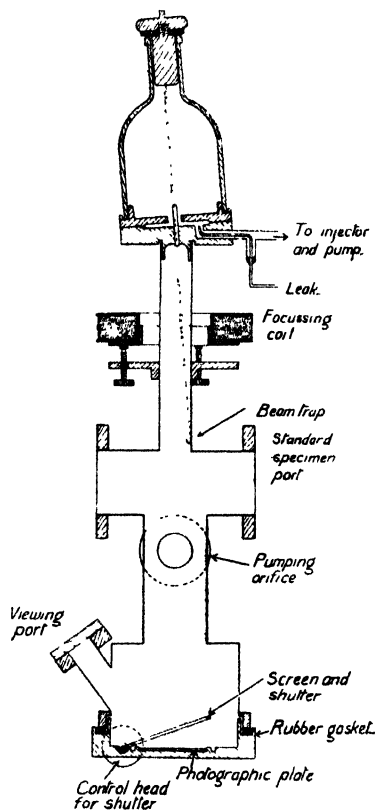


FIG. 5.—Small Camera.

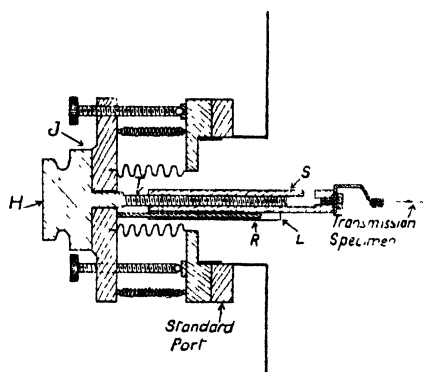


FIG. 6.—Specimen Carrier.

On the lower surface of the combined shutter and fluorescent screen is a rectangular flange fitting into a corresponding groove in the brass block and surrounding the photographic plate. This renders

the camera light-tight and obviates the necessity for using the instrument in a laboratory which must be completely darkened.

The axis of the discharge chamber is so strongly tilted by the steeply wedge-shaped anode block, that the undeflected electron and molecular beams impinge upon the wall of the tube above the specimen. A small cobalt steel bar magnet can be adjusted into such a position below the anode diaphragm that the most intense part of the wide magnetic spectrum obtained with the unsmoothed and unrectified output of an induction coil follows approximately the axis of the diffraction section. A diaphragm held in the second specimen carrier serves to screen off the unwanted polychromatic electrons.

Owing to the small volume of the instrument, a high-capacity evacuating system is unnecessary, and a quartz three-stage mercury vapour pump backed by a "Hyvac" rotary oil pump is found to be quite satisfactory.

Method of Operation.—The method of operation is similar for both instruments. The specimen, clamped in a suitable holder, is screwed to the stem of the lower specimen carrier; the camera is loaded and the apparatus pumped down. The high-tension current is then switched on and the pressure in the leak reservoir so regulated that the discharge tube is working at a convenient voltage, usually between 45 and 60 KV. The focussing coil current is adjusted and the electron beam biased to fall on the specimen by tilting the coils. In the case of examination by transmission, the tilt of the focussing coils is varied continuously in order to explore the specimen systematically over the whole of its area; in reflection experiments, however, the specimen is adjusted before exploration until the angle of incidence is as small as possible. When that part of the specimen which gives the best diffraction pattern has been found, the adjustable diaphragm is brought into position immediately above the specimen and the photographic plate is exposed. The voltage at which the discharge tube is working is measured by means of the sphere-gap voltmeter immediately before and after exposure. After switching off the high-tension current, air is admitted to the camera without allowing the diffusion pump to cool, and the camera and specimen carrier reloaded; whereupon the apparatus can be re-evacuated whilst the exposed plate is being developed. The complete cycle of operations from the exposure of one plate to the recording of the pattern from another specimen can be completed in about five minutes. The normal time of exposure is one-fifth seconds.

The Preparation of Specimens.

It is hardly necessary to stress the importance of the preparation of specimens for examination by electron diffraction. With a view to developing a reliable and simple technique for this purpose, the methods hitherto in use have been closely examined in this laboratory and modifications introduced where necessary, and an account will now be given of those methods which have stood the test of experience.

Transmission Specimens.

The Specimen Support.—The supporting diaphragm used by other workers must either be so small as unduly to restrict the area of specimen available for examination, or so large as to subject the specimen to excessive strain during preparation and liability to accidental injury in use. A fine wire gauze as support in place of a diaphragm overcomes these objections.⁸ An 80 mesh per inch nickel gauze with an average mesh aperture of 0.2 mm². is readily procurable in the form of 2.5 cm. wide selvaged strip. Where, for chemical or other reasons, the use of nickel is inadvisable, a similar gauze of platinum or gold serves as support. A useful total area for most purposes is about 1 square inch. A wire

spot-welded to one edge of the gauze makes for convenience in handling. The material to be examined may be deposited either directly in such a manner as to bridge the meshes, or on a thin cellulosic film, itself supported by the gauze. In cases where the specimen is particularly fragile, or is likely to be required for further examination, it is advisable to spot-weld over it a second piece of gauze; in view of the fineness of the wire it is immaterial whether the meshes in the two gauzes register or not. Specimens protected in this manner can be handled without special precautions and can be stored in envelopes. The diffraction pattern from a suitable cellulosic substrate should consist of two or three faint and ill-defined haloes with but little general background. Some cellulosic films exhibit a pronounced polycrystalline (Fig. 30) or even single crystal (Fig. 31) structure, and the use of such films as supports might easily lead to confusion. Dauvillier⁴ and Kirchner⁵ found that both the method of preparation and age of a celluloid film affect its structure. Thin coherent films in the amorphous state, or nearly so, can readily be cast by pouring a few drops of a dilute alcohol-ether solution of acetate cellulose on water contained in a wide dish. Dust particles on the surface of the water are swept to the edges of the dish by the solvent vapour; thus the resulting film, which may be easily picked up on gauze, is free from holes. With amyl acetate as solvent the films often exhibit a more or less pronounced crystalline structure (Figs. 30 and 31).

Metal Specimens.

"Flashing."—Transmission specimens of the more volatile and particularly of the reactive metals are best formed by "flashing" from a 30 S.W.G. tungsten filament on to cellulosic gauze in the evacuated diffraction camera, the leak system being fed with the appropriate inert gas.⁶ The most suitable method of charging the filament depends upon the nature of the metal. In the case of zinc, the bend of a U-shaped filament is quickly dipped into the molten metal and withdrawn into a reducing atmosphere. Wires of easily volatilised and reactive metals such as aluminium, magnesium, barium, lithium (Fig. 34) and sodium, are wrapped round the filament; with suitable adjustment of the "flashing" current, only the metal volatilises and is deposited on the specimen support, the slag remaining behind on the filament. In the case of potassium a small pellet is well kneaded in several changes of volatile hydrocarbon in order to remove the heavy hydrocarbons, and then moulded round the filament and transferred to the diffraction camera, previously filled with hydrogen purified by bubbling through liquid sodium-potassium alloy. The more refractory metals may be either "flashed" directly, or slowly evaporated in the camera, by heating the appropriate filament. Thus tungsten is best "flashed," whilst a silver wire evaporates sufficiently readily, even when heated to well below the melting-point.

Foil-thinning.—Au, Ag, Pt, Sn, Zn, Al, Cu and possibly other metals are commercially obtainable as foils which can be thinned down by suitable etching and then mounted on gauze. The thinner foils are floated on a bath of etching reagent and washed after thinning by floating on several changes of distilled water. For transferring the film from one bath to another, it is convenient to use a gauze support. The thicker foils are best reduced by total immersion in the etching bath, this being easily done if the foil is enclosed between two layers of gauze spot-welded together at the edges. Indeed, this procedure so greatly simplifies handling that its general adoption is to be recommended in the case of the more fragile metal films. As a rule it is advisable to select as etching reagent one which avoids evolution of gas; for example, it is preferable to thin gold leaf with a solution of potassium cyanide rather than with *aqua regia*.

Cathodic Sputtering.—Cathodic sputtering on to cellulosic gauze affords a convenient method for obtaining excellent transmission specimens of almost any metal.¹⁰ Sputtering is best carried out in dried and purified

argon.⁷ By varying the sputtering conditions, in particular the discharge current and gas pressure, it is possible to exercise considerable control on the arrangement and size of the crystals.²⁰ If desired, the cellulosic support can be dissolved away and the metal film transferred directly to a gauze (Figs. 82 and 83).

Colloid Precipitation.—Colloidal solutions of metals formed by Faraday's⁸ arc dispersion method or by Svedberg's⁹ modification yield good crystalline transmission specimens when a drop of the solution is dried out on cellulosic gauze (Figs. 26, 27, 82 and 83). The more noble metals are best dispersed in water or alcohol; in other cases a volatile liquid hydrocarbon is to be preferred.

Chemical Deposition.—Films of silver (Fig. 71), gold, platinum, and possibly other metals can be readily formed by playing a flame on to the surface of the corresponding "silvering" solution, the film being picked up on gauze and washed in the usual manner.

Electrodeposition.—Another useful way of preparing transmission specimens of a wide range of metals is by electrodeposition, two methods having been developed in this laboratory by Mr. C. H. Sun. In the one, the metal is deposited on a substrate of metal foil which is subsequently dissolved away by a suitable reagent. For example, nickel is deposited on a gold leaf cathode floating on a nickel sulphate-sodium citrate bath, the gold being subsequently removed by floating on a dilute potassium cyanide solution. The second method, in effect a modification of the first, but applicable to a much wider range of metals, consists in plating a stainless steel surface with a relatively thick film of basis metal, followed by a suitable thickness of the required metal. The composite film is then stripped off, the basis dissolved away, and the film mounted on gauze and washed in the usual manner. Stripping is easily effected after loosening an edge or corner of the film with a sharp knife. In Table I. is given a list

TABLE I.

Metal.	Fig.	Bath.	Basis Metal	Etching Reagent.
Iron . .	68	Ferrous Ammonium Sulphate	Cu	6N KCN
Cobalt . .	69	Sulphate	Cu	6N KCN
Nickel . .	67	Sulphate	{ Cu 6N KCN Cd 4N NH ₄ NO ₃ Zn 2N HCl	
Copper . .	90	Cyanide	Cd	4N NH ₄ NO ₃
Silver . .	58, 59, 60	Cyanide	{ Cu 3N HNO ₃ Ni 6N HNO ₃ Bi 6N HNO ₃ Sn 3N HNO ₃ Fe 3N HNO ₃	
Gold . .	84, 85, 91	Cyanide	{ Cu 3N HNO ₃ Ni 6N HNO ₃ Bi 6N HNO ₃ Sn 3N HNO ₃ Fe 3N HNO ₃	
Chromium .	77	Chromic Acid	{ Ni 6N HNO ₃ Cu 3N HNO ₃ Bi 6N HNO ₃ Sn 3N HNO ₃ Fe 3N HNO ₃	
	76		Cu	6N KCN
	81		{ Au 6N KCN Cu 6N KCN	
	79 and 80		{ Cu 6N KCN Ni 6N HNO ₃ Cu 3N HNO ₃ Bi 6N HNO ₃ Sn 3N HNO ₃	
Tungsten .	88	Sodium Tungstate	Cu	6N KCN
Bismuth . .	66	Perchlorate	Cu	6N KCN
Arsenic . .	37	Cyanide	Au	6N KCN
Antimony .	36	Acid Trichloride	{ Au 6N KCN Cu 6N KCN	
	89	Schlippe's Salt	Cu	6N KCN
Tin . .	64 and 65	Alkaline Chloride	{ Ni 6N HNO ₃ Cu 3N HNO ₃ Bi 6N HNO ₃ Sn 3N HNO ₃	
Platinum .	61, 62, 63	Phosphate		

of the metals which have so far been prepared for transmission purposes by this method, together with the corresponding basis metals, baths and etching reagents.

Non-metallic and Compound Specimens.

In addition to "flashing," colloid precipitation and chemical deposition, several other convenient methods are available for the preparation of transmission specimens of the metalloids and of compounds, both inorganic and organic. These are (i) distillation in air or *in vacuo*,²¹ (ii) deposition of soots and dusts, (iii) crystallisation from solvents, (iv) casting of thin films, (v) gas-etching of metal or other films, (vi) slag-skimming,²² and (vii) cleaving of crystal fragments.

Metalloids.—The preparation of transmission specimens of the non-metallic elements presents, as a rule, greater difficulties than in the case of metals. Sulphur, and to a lesser extent phosphorus, specimens are prone to charge up in the electron beam, whilst iodine volatilises in the diffraction camera. The tendency to charge up is greatly reduced, however, when the material forms a continuous film in direct contact with the gauze. We have obtained satisfactory selenium, tellurium and arsenic films by "flashing" *in vacuo* on to cellulosized gauze and from colloidal solutions. Good specimens of the various forms of carbon are readily prepared and afford a variety of diffraction patterns of great interest. Soots should be collected directly on gauze, because they often yield patterns somewhat resembling the normal halo pattern of the cellulosic substrate. Graphite when deposited from the aqueous colloidal solution ("aquadag") on cellulosized gauze gives an exceptionally brilliant pattern (Fig. 52). A graphite flake sufficiently thin to yield a single crystal spot pattern can be cleaved from a natural crystal.

Oxides.—Sn, Pb, Zn, Al, Co, Ni, Cu, Sb and Tl foils, prepared by one of the above methods and mounted between two gauzes, all yield characteristic oxide patterns after drawing through a Bunsen flame at a suitable rate to avoid melting or volatilising the foil (Figs. 48, 49 and 50). In most cases there is no need for the original foil to be thin enough to transmit electrons. For example, ordinary tin or aluminium wrapping foils are quite satisfactory without further thinning. A refinement of this method consists in heating the metal specimen to a known temperature in a furnace in an oxygen atmosphere. Many other compounds can be obtained by immersing metallic films in the appropriate gas at a suitable temperature.

In the case of the oxides of lead, zinc, cadmium, bismuth and tin, a 0.5 cm. wire loop is usually spanned on withdrawal from the molten metal by a comparatively thick metal film which, on cooling, forms cracks bridged by oxide and affording satisfactory patterns.¹⁰ The oxide can also be skimmed from the surface of the melt by a wire loop or preferably by gauze. As a rule both these methods yield specimens giving composite metal-metal oxide patterns in which that due to the metal is more or less prominent; when an oxide specimen alone is required, the oxide smoke may be condensed on gauze.^{6, 11} Certain metals, such as magnesium, zinc and cadmium, when ignited in air, burn with the production of an oxide smoke easily collected on a gauze. A much more general and effective method, however, consists in producing the oxide smoke by burning a low-tension arc between electrodes of the metal either in air, or in oxygen, should the presence of nitrogen be undesirable (Fig. 38).

Another useful method consists in impregnating a gauze with a soluble salt which decomposes on heating to form the oxide; for example, remarkably good specimens of thoria can be obtained in this manner from the nitrate (Fig. 39).

Other Compounds.—Transmission specimens of most organic and inorganic compounds which will withstand a high vacuum, can be prepared by "flashing" on to cellulosized gauze from a platinum or tungsten filament.

The filament is charged by withdrawing either from a melt or hot saturated solution or coated by painting with an aqueous suspension,¹⁰ and "flashing" is carried out in air or *in vacuo* according to the nature of the substance. Thus we have experienced no difficulty in preparing sodium chloride and calcium fluoride specimens by evaporation *in vacuo*; on the other hand, some compounds, for example cadmium iodide, anthracene (Fig. 32), and mercuric chloride, give the best specimens when "flashed" in air. Many compounds boiling or subliming *in vacuo* below about 600° C. can be distilled in a quartz test-tube and condensed on the support without destroying the cellulose by excessive heating.

Crystallisation from a solvent forms another method of wide application. In practice, withdrawing a gauze from a hot saturated solution of the substance followed by rapid evaporation usually yields a good polycrystalline film, and excellent single crystal transmission specimens can often be obtained in this manner. With the more sparingly soluble substances, drying out a drop of the solution (or suspension) on cellulosized gauze is more effective. The solution may also be sprayed on with an "atomiser" or painted on with a brush.

Specimens of many organic substances are readily prepared by spreading a solution out on the surface of a suitable liquid. For example, palmitic, stearic (Fig. 33) and lauric acid solutions in benzene, poured on to water or mercury, form films which can be picked up on gauze and afford remarkable patterns.¹²

Specimens of refractory materials can be obtained by fine grinding, preferably in a ball mill, and drying out a drop of the suspension on cellulosized gauze. The scope of this method is by no means limited to refractory substances; practically any finely powdered material can be dealt with in this manner. The range of particle size usually obtained, however, is wide, with the result that the diffraction patterns afforded by such specimens are often ill-defined and show much background. In certain cases, ball-milling does not lead to a satisfactory result; for instance, to obtain a ring pattern of mica, the powder is best prepared by rubbing two freshly-cleaved surfaces together (Fig. 35).

"Reflection" Specimens.

Although it is possible, by one or other of the methods outlined above, to obtain transmission specimens of practically any substance which will withstand a high vacuum, there are many cases in which it is undesirable to separate the film to be examined from the matrix out of which it has been formed. Thus, a clean copper surface oxidises slowly in air at room temperature, and rapidly when heated; the oxide film can be stripped off with a KCN solution and mounted on gauze for transmission purposes. The transmission pattern from such a film, however, can and often does differ from that afforded by the oxide on the copper surface, thus showing that the process of stripping has materially effected the structure of the oxide film. The Thomson-Shinohara¹⁴ grazing incidence or "reflection" method of electron diffraction permits of the examination of surface structures without disturbing the intimate relationship between surface layer and matrix, and herein lies, perhaps, the outstanding advantage of this method. Furthermore, not only is it possible to prepare reflection specimens of practically any substance by deposition on a flat support by one or other of the methods available for transmission specimens, but we can also examine by "reflection" substances, in particular liquids, which are virtually inaccessible to the transmission method. Thomson¹⁵ has shown that "reflection" of an electron beam at grazing incidence by a polycrystalline surface is, in general, essentially a case of transmission through minute crystallites projecting out of the surface.

The Specimen Support.—The specimen support is either the *matrix* upon and out of which the specimen has been formed, or a *substrate* upon which the specimen has been deposited. The substrate itself may or may

not govern the properties of the specimen layer in some important respect or other; accordingly we must distinguish between active and inert substrates.

It is only in the case of a plane surface that the effective specimen area can equal that of the support; hence where possible this should consist of a disc, preferably with plane-parallel faces for convenience in mounting in the specimen holder. Experience has shown that in general a disc diameter between about 1 and 2.5 cm. is suitable. Substances of low electrical conductivity are preferably supported on metal substrates in order to minimise charging-up effects. The choice of material in the case of a support intended to act as matrix or active substrate is determined by the objects and experimental requirements of the particular investigation.

The Specimen.—"Reflection" specimens can be prepared by the methods previously found suitable in the case of transmission specimens, the gauze or cellulosed gauze support being replaced by a flat disc which, however, may act either as an inert or active substrate. In addition, by using the support as matrix, further methods become available. Thus, the surface may be subjected to chemical attack, with or without removal of the products; indeed, it has become a matter of general experience that practically any smooth surface will give rise to a diffraction pattern after having undergone chemical attack (Figs. 24, 28, 29, 51, 74, and 75).

The matrix may also be acted upon physically with the object of revealing either its structure or the effect of such action upon its structure. For example, a highly polished metal surface is practically devoid of organised structure and has in consequence certain remarkable properties not possessed by the surface in the crystalline state.²⁸ Again, in many metal surfaces the crystal arrangement is unfavourable for observation by electron diffraction, but scratching with a suitable abrasive suffices to raise out of the surface crystal fragments sufficiently thin to transmit electrons (Figs. 56 and 57).

Liquids and floating scums, films or slags can be examined at grazing incidence, in the manner first suggested by Trillat¹⁸ for X-rays, advantage being taken of the convexity of the surface of a liquid contained in a brim-full cup or of a drop on an unwetted surface; or the support can be wetted with a thin film of liquid, either as such or dissolved in a volatile solvent, thus obviating the need for a horizontal camera.

The Interpretation of Electron Diffraction Patterns.

In spite of the fundamental differences between X-rays and electrons and their modes of interaction with atoms, the pattern yielded by a polycrystalline specimen, *e.g.*, Fig. 25, often bears so striking a resemblance to the corresponding X-ray powder pattern that at first sight it might be supposed that the mechanism of their formation was similar. It is also true that the analysis of an electron diffraction ring pattern in some respects can, and often does, conform to that of the corresponding X-ray powder pattern, but in others the differences are such that it would be dangerous to press the analogy between the two methods. For this reason, it is best to approach the interpretation of the patterns from the electron diffraction aspect, rather than from that of X-ray analysis; and this is best achieved by considering in the first place the diffraction of electrons by single crystals, where the phenomena observed differ greatly from those obtained with X-rays.

Electron Diffraction by Reflection from a Crystal Face.—

Since the path difference between co-operating rays must be an integral number of wave-lengths, the condition for diffraction of a monochromatic beam of wave-length λ by a line grating of constant a is

$$a(\cos \alpha - \cos \alpha_0) = h\lambda,$$

where α_0 and α are the directions of the incident and reinforced beams respectively, and h is an integer. In the case of a plane or cross-grating, two such conditions must be fulfilled simultaneously, and with the three-dimensional grating or space-lattice three such simultaneous equations, known as the Laue conditions, must be satisfied. The Laue conditions for diffraction by a space lattice are so stringent that with a monochromatic beam no diffracted ray will appear except for certain definite angles of incidence. If, on the other hand, only two of the Laue conditions have to be satisfied, as in the case of the cross-grating, there will be a series of diffracted beams for all angles of incidence.

The zero order rays diffracted by a line grating normal to the beam sweep out a plane normal to the grating and containing the beam, whilst rays of higher order describe cones of the appropriate semi-apex angles $\alpha_1, \alpha_2, \alpha_3$, etc., about the grating. In electron diffraction, where the beam is always normal, or nearly so, to the screen, the corresponding diffraction pattern will therefore consist of a straight line passing through the undeflected spot and normal to the projection of the grating on the screen, together with hyperbolæ which, owing to the small angles of diffraction involved, are in practice equivalent to a series of equidistant and parallel straight lines on either side of the zero order diffraction. If the grating is inclined to the beam, all the diffractions, including the zero order, change with progressive inclination through the series of conic sections to ellipses until, finally, with the grating in line with the beam, the pattern consists of concentric circles described about the undeflected spot (zero order diffraction), the so-called Laue circles.

The resolving power of a line grating is not only determined by the number of scattering centres, but also depends upon its inclination to the beam, being least when the grating and beam coincide. Thus, with $\lambda = 0.05 \text{ \AA}$, $a = 5 \text{ \AA}$. and 20 scattering centres in a grating normal to the beam, it can easily be shown that the resolution is practically perfect. When the grating is in line with the beam, however, the path difference between waves scattered at an angle ϕ by successive atoms in the line grating is

$$a(\cos \phi - 1) \simeq a\phi^2/2.$$

Thus, the corresponding phase difference

$$\delta = a\phi^2\pi/\lambda.$$

Summing the waves scattered in this direction by all the n atoms of the grating, we have the resultant intensity factor

$$A^2 \cdot \sin^2 \frac{n\delta}{2} / \sin^2 \frac{\delta}{2},$$

where A is the scattering power of a single atom.

The minima are given by

$$n\delta/2 = N\pi,$$

where N is an integer; and the principal maxima by

$$\delta/2 = N\pi.$$

Hence the angular radius ϕ_0 of the zero principal maximum is given by

$$\frac{n}{2} \cdot \frac{a\phi_0^2 \cdot \pi}{\lambda} = \pi,$$

i.e.,

$$\phi_0 = \sqrt{2\lambda/na} = \sqrt{2\lambda(n-1)/nT},$$

where T is the length of the grating.

Thus, for the dimensions given and a camera length of 50 cms., instead of the zero order diffraction spot being of the same cross-section as the effective electron beam, as it would be with maximum resolving power, it will now have a radius of 1.5 cm.

In general, with monochromatic X-rays impinging on a single crystal, no diffraction will occur except with those settings satisfying the three Laue conditions, but with electrons at grazing incidence, patterns of spots, lines and bands superimposed upon a more or less intense background of general scattering are obtained. The apparent complexity of the phenomena is perhaps best elucidated by a consideration of the patterns obtained from a single crystal of known simple structure possessing either two well-defined and different natural faces, or one such face and a different cleavage plane, as is the case with fluorite where the cubic unit cell contains four molecules—the calcium atoms at the corners and face-centres of the cube, and the fluorine atoms at the centres of the eight equal cubes into which the unit can be divided.

Fig. 7 is the pattern yielded by a cube face grazed by the electron beam parallel to a cube edge.

The pattern of spots arranged at the corners of squares can be explained as follows.²⁴ Rows of atoms normal to the beam and parallel to the crystal face form line gratings of high resolving power, the diffraction cones of which would cut the screen in the sharp lines of direction *AB* (Fig. 8). Owing to the low penetrating power of the electrons, the effective length of the line gratings formed by atom rows normal to both beam and crystal face will be small and the resolving power low; consequently, the corresponding pattern will consist of broad bands at right-angles to *AB*.^{*} Finally, the atom rows in, or nearly in, the direction of the beam will have a poor resolving power, as shown by the Laue circle haloes in Fig. 8. Intersections common to the three patterns give the directions of the diffracted rays yielding the spot pattern observed in Fig. 7, and in this manner we can account not only for the positions of the spots, but also for their shape. Bearing in mind the consequences of the fact that the spot pattern is obtained only because two Laue conditions are partially relaxed, the indexing of the spots is carried out as in the case of X-rays.

The bands, and black and white lines (Kikuchi lines) have no counterpart in X-ray structure analysis. It is generally agreed that they are due to multiple scattering.

The origins of the Kikuchi lines can be determined as follows. To

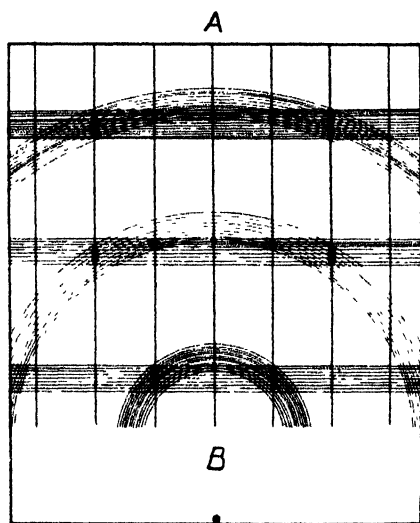


FIG. 8.

* Owing to the effect of inner potential, these bands will not be quite equidistant.

Since the electron beam is normal to, and meets the screen at O_2 , where $OO_2 = L$, the intersection with the screen of the (hkl) plane passing through O is obtained by putting $y = -L$, whence

$$C_1z = -A_1x + B_1L.$$

We now postulate a divergent beam of electrons, of wave-length λ in the crystal, the intensity falling off with deviation from the main beam direction, and suppose that these electrons be reflected at the various net planes according to Bragg's law. Thus we assume, for

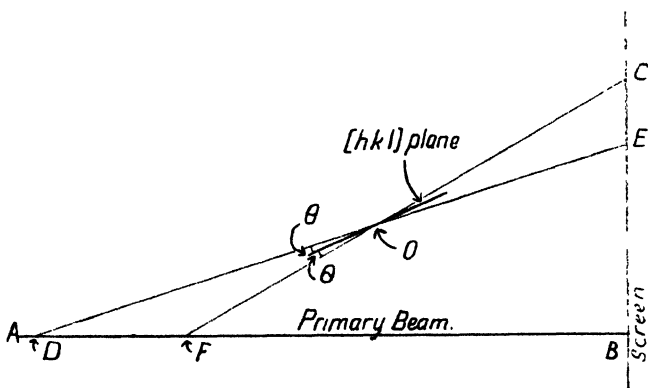


FIG. 10a.

reasons given below, that both primary and secondary scatterings are elastic. The rays diffracted by the (hkl) plane will form a cone of semi-apex angle $90^\circ - \theta$ round the (hkl) normal and intersecting the screen in hyperbolæ given by

$$(A_1x + B_1y + C_1z)^2 = (x^2 + y^2 + z^2) \cdot \left(\frac{n\lambda}{2d}\right)^2,$$

$$y = -L,$$

where d is the (hkl) spacing, and n the order of the diffraction. In Fig.

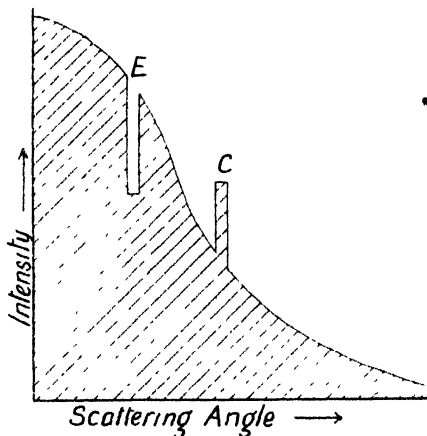


FIG. 10b.

10a let AB be the direction of the primary beam and CF , ED the cross-section of the cone of rays diffracted by the (hkl) planes. Then, from Bragg's law, it follows that rays which would have been received at C and E are diffracted by the (hkl) planes to E and C respectively. Now, if the rays DO and FO are of equal intensity, no resultant effect due to secondary scattering will be observed; but if the intensity falls off with deviation from the main beam direction, for example, in a manner similar to that given by the continuous curve in Fig. 10b, the secondary diffraction

will lead to an increase in the number of electrons received at C and a decrease in the number arriving at E . Hence, the hyperbolæ passing through C and E respectively, will be observed on the fluorescent screen

as black and white lines with regard to the neighbouring back-ground.* These are the Kikuchi lines and are given by

$$A_1x + C_1z - B_1L = \pm (x^2 + z^2 + L^2)^{\frac{1}{2}} \cdot \frac{n\lambda}{2d}.$$

At small angles, when $(x^2 + z^2) \ll L^2$, this becomes

$$C_1z \approx -A_1x + \left(B_1L \pm \frac{n\lambda L}{2d}\right). \quad (5)$$

If the origin of co-ordinates on the screen is changed from O_2 , the point of intersection of the main beam, to O_1 , the point of intersection of Y_1O produced, the equation of the Kikuchi lines becomes

$$C_1z = -A_1x + \left(\frac{B_2L}{\cos \psi} \pm \frac{n\lambda L}{2d}\right),$$

or, for small values of ψ ,

$$C_2z = -A_2x + \left(B_2L \pm \frac{n\lambda L}{2d}\right). \quad (6)$$

Thus, if the angle of grazing incidence, ψ , is increased slightly from zero, the Kikuchi line pattern moves as a whole through a distance $L \tan \psi$ parallel to the Z axis. Similarly, it can be shown that a small change $\Delta\phi$ in the azimuth results in a bodily movement of the line pattern through a distance $L \tan \Delta\phi / \cos \psi$, parallel to the X axis of the screen. Thus, in the analysis of Kikuchi line patterns, the effect of a small angle of incidence, ψ , need not be considered, if the origin of the screen co-ordinates is taken in the line of intersection of the (uvw) plane with the screen; again, if the azimuth is near a known rational azimuth, ϕ , corresponding to a zone axis in the (uvw) plane, this value of ϕ can be inserted in the equation for the Kikuchi lines, and the origin of screen co-ordinates taken as the point of intersection of the zone axis with the plate.

The fundamental equation for the analysis of Kikuchi line patterns is therefore

$$C_2z = -A_2x + \left(B_2L \pm \frac{n\lambda L}{2d}\right), \quad (7)$$

where $A_2 = A_3 \cos \phi - B_3 \sin \phi$,
 $B_2 = A_3 \sin \phi + B_3 \cos \phi$,
 $C_2 = C_3$;

and $A_3 = (\lambda W - \nu U) / \sqrt{1 - V^2}$,
 $B_3 = \{-\lambda UV + \mu(1 - V^2) - \nu VW\} / \sqrt{1 - V^2}$,
 $C_3 = \lambda U + \mu V + \nu W$;

and $n\lambda L/d$ is the distance between the pair of Kikuchi lines.

If the crystal possesses an inner potential, E , the electrons will behave as if it had a refractive index, $\mu = \sqrt{1 + E/V}$, where V is the accelerating potential of the beam. In what follows, we continue to assume that all scattering, both primary and secondary, is elastic. From Snell's law, it

* "Black" or "white" is used here throughout in terms of the screen or positive. Note that the positive is the mirror image of the pattern as viewed in the screen from above.

follows that the ordinate, z , of any point on the Kikuchi lines given by (7) is then changed to z' , where

$$z^2 = \left(1 + \frac{E}{V}\right)z'^2 + \frac{E}{V}(x^2 + L^2),$$

$$\text{or} \quad z'^2 = z^2 - \frac{E}{V} \cdot L^2, \quad . \quad . \quad . \quad . \quad . \quad (8)$$

when $x \ll L$ and $E \ll V$. Thus, if the equation of a Kikuchi line is $z = mx + c$ when $E = 0$, then for finite values of E the corresponding Kikuchi line becomes the hyperbola

$$z^2 - m^2x^2 - 2mcx + \left(\frac{E}{V}L^2 - c^2\right) = 0 \quad . \quad . \quad (9)$$

which is rapidly asymptotic to $z = mx + c$. The effect of an inner potential of 10 volts when $V = 45$ KV. and $L = 28$ cm. is shown in Table II.

TABLE II.

Thus the effect of inner potential upon the Kikuchi lines is small, except for low values of z , *i.e.*, for the regions near the intersection of the plane of the crystal face with the screen. It is also easy to see that the effect is wholly negligible in the case of transmission through a single crystal where the angles made by the external faces with the beam are large.

Planes parallel, or nearly so, to the beam give rise to the remarkable bands. As far as we know, no satisfactory complete explanation of these bands has been given.

z in cms.	z' in cms.	$\frac{z - z'}{z}$
7	6.988	0.0017
6	5.985	0.0025
5	4.983	0.0034
4	3.979	0.0041
3	2.971	0.0097
2	1.956	0.0220
1	0.909	0.0910
0.5	0.028	0.9448
0.30	0.000	1.0000

The main features of the four patterns, Figs. 7, 11, 12 and 13, obtained from the fluorite cube face with different azimuthal settings, have been indexed in accordance with the above scheme. The effect of a small clockwise change in azimuth is shown by Fig. 11, which is simply equivalent to a tangential displacement of the line pattern of Fig. 7 in the same direction. The spot pattern, on the other hand, has followed the Laue ring displacements and radial changes. Fig. 12, taken in the $26^\circ 34'$ azimuth, *i.e.*, along the (210) plane direction, exhibits a corresponding asymmetry in the Kikuchi pattern. With $\phi = 45^\circ$ (Fig. 13), *i.e.*, looking along the cube face diagonal, the pattern symmetry is restored. Figs. 14, 15 and 16 were obtained with the beam grazing a (111) cleavage face at azimuths 0° , 30° and 60° respectively, where at 0° the k axis is in the plane of incidence and pointing towards the electron source. Symmetrical but otherwise different patterns are obtained at 0° (Fig. 14) and at 60° (Fig. 16), and these are repeated at 120° intervals. In Fig. 15 ($\phi = 30^\circ$) the pattern is symmetrical about the 100 band, but asymmetric about the z axis.

It will be seen that the structure amplitude restrictions for the known structure of fluorite are obeyed throughout in the relative intensities of the Kikuchi lines. For example, in the 100 set, Fig. 7, only even orders are present, and the 2nd and 6th orders are weak, whilst the 4th and 8th are strong; and in general throughout the fluorite patterns odd orders occur only for planes of which all indices are odd. Furthermore,

the separations of Kikuchi line pairs, except in the region affected by inner potential, agree within about 2 per cent., *i.e.*, the error due to voltage measurement, with those corresponding to the known lattice dimensions.

The black and white parabolæ so prominent in the patterns, and particularly well-defined in Figs. 7 and 16, are envelopes of Kikuchi lines. For reflection from the cube face, equation (7) reduces to

$$lz = -Ax + \left[BL \pm \frac{n\lambda L}{2a} \cdot \Sigma h^2 \right],$$

$$\text{or} \quad lz = -Ax + \left[BL \pm \frac{n\lambda L}{2a} (l^2 + A^2 + B^2) \right],$$

where $A = h \cos \phi - k \sin \phi$,
and $B = h \sin \phi + k \cos \phi$.

Thus the envelopes with respect to l are the parabolæ given by

$$\pm z^2 = \frac{2n\lambda L}{a} \left[-Ax + BL \pm \frac{n\lambda L}{2a} (A^2 + B^2) \right]; \quad (10)$$

whilst those with respect to A form the system of parabolæ

$$\pm x^2 = \frac{2n\lambda L}{a} \left[-lz + BL \pm \frac{n\lambda L}{2a} (A^2 + l^2) \right]. \quad (11)$$

The envelopes of both these systems of parabolæ in terms of A and l respectively are the circles (approximately 3.7 cm. radius in Fig. 7), so well marked in most of the fluorite patterns,

$$x^2 + z^2 = \pm \frac{2n\lambda L}{a} \left[BL \pm \frac{n\lambda L}{2a} B^2 \right]. \quad (12)$$

The definition of the patterns, and more particularly that of Figs. 7 and 16, is such that both primary and secondary envelopes are clearly seen to consist of short straight lines.

For the azimuthal settings in Figs. 7, 12 and 13 the values of A and B are:—

Fig. 7: $\phi = 0^\circ$: $A = h$, and $B = k$;

Fig. 12: $\phi = 26^\circ 34'$: $A = \frac{2h-k}{\sqrt{5}}$, and $B = \frac{h+2k}{\sqrt{5}}$;

and Fig. 13: $\phi = 45^\circ$: $A = \frac{h-k}{\sqrt{2}}$, and $B = \frac{h+k}{\sqrt{2}}$.

Substitution of these values in equations (10) and (11) gives parabolæ in positions as recorded in the patterns. Parabolæ with a common axis in z and touching the innermost circular envelope (Fig. 7) are due to planes for which $k = 1$. The other parameter, l , distinguishing the members of this series, has only odd values, which accords with the structure. Parabolæ with inclined axes as in Fig. 12, are readily accounted for in a similar manner.

In the case of the cleavage plane reflections, the parabolic envelopes with respect to the appropriate C and A factors are

$$\pm z^2 = \frac{2n\lambda L}{a\sqrt{6}} \left[-Ax + BL \pm \frac{n\lambda L}{a2\sqrt{6}} (A^2 + B^2) \right],$$

and $\pm x^2 = \frac{2n\lambda L}{a\sqrt{6}} \left[-Cz + BL \pm \frac{n\lambda L}{a2\sqrt{6}} (B^2 + C^2) \right]$ respectively;

and the circular envelopes of both these systems in terms of A and C respectively are given by

$$x^2 + z^2 = \pm \frac{2n\lambda L}{a\sqrt{6}} \left[BL \pm \frac{n\lambda LB^2}{a2\sqrt{6}} \right].$$

As previously, the envelopes are obtained by substitution of the following values of B and C in these equations:—

Fig. 14: $\phi = 0^\circ$: — $A = \sqrt{3}(l - h)$ and $B = 2k - h - l$;

Fig. 15: $\phi = 30^\circ$: — $A = k + l - 2h$ and $B = \sqrt{3}(k - l)$;

and Fig. 16: $\phi = 60^\circ$: — $A = \sqrt{3}(k - h)$ and $B = h + k - 2l$.

In all these cases $C = \sqrt{2}(h + k + l)$. It may be noted that for parabolæ enveloping the innermost circle, with $\phi = 0^\circ$, we have

$$2nk - nh - nl = 2 \text{ or } \Sigma nh = 3nk - 2.$$

Since nk must be an integer, Σnh can only have the values 1, 4, 7, etc.; thus determining which parabolæ of this type can appear. Similarly, for $\phi = 60^\circ$, $\Sigma nh = 3nl + 2$, and only those parabolæ for which $\Sigma nh = 2, 5, 8$, etc., can occur. Comparison with Figs. 14 and 16 shows how excellent is the agreement.

In both the cube and cleavage face reflections, the radii of the circular envelopes are the same as those of the circular zones of reinforcement to be expected with the beam parallel to rows of lattice points. Thus, if we postulate that, when the $(H\bar{K}O)$ plane is in the plane of incidence for cube face reflection, a secondary beam is parallel to the row $[-K, H, O]$, i.e., the co-ordinates of any point on the row referred to the hkl axes are in the ratio $-K : H : O$, and the lattice-point spacing in the row is $a\sqrt{H^2 + K^2}$, then the circular zones of reinforcement have radii given with sufficient accuracy for small scattering angles by

$$r = \sqrt{\frac{2n\lambda L^2}{a\sqrt{H^2 + K^2}}}. \quad (13)$$

The radii of the circular envelopes can, however, be obtained by substituting in equation (12)

$$\begin{aligned} B &= \frac{hK + kH}{\sqrt{H^2 + K^2}} \\ &= N/\sqrt{H^2 + K^2}, \end{aligned}$$

where N is any integer; whence, to the previous sufficient degree of accuracy, the radii of the circular envelopes are given by

$$r = \sqrt{\frac{2n\lambda L^2}{a\sqrt{H^2 + K^2}}}.$$

It can be shown in a similar manner that this is also true for the circles obtained in the cleavage plane reflection patterns.

Thus, two explanations, both agreeing quantitatively with the observed radii, can be put forward to account for the origin of these circles. We regard them as secondary envelopes of the Kikuchi lines, whilst Emslie¹⁷ and Tillman²⁴ attribute them to secondary coherent scattering by atom rows nearly parallel to the primary beam. It is, however, difficult to account for the definition observed in the fluorite patterns by Emslie's hypothesis, because there seems to be little reason for supposing that the

producing beam would be limited to the direction parallel to the atom rows. Also, according to this one-dimensional view, the circles should be true circles, but the definition in the patterns enables it to be seen clearly that they are really polygons, and therefore secondary envelopes of the Kikuchi lines. Another circle, or rather polygon, of similar origin, of radius 2.1 cms. and described about the intersection of the medians of the 121, 110 and 211 bands can be seen in Fig. 16. In the region remote from the undeflected spot this polygon is made up of white Kikuchi lines, but has black Kikuchi lines enveloping the other half. It seems to us that these facts negative the one-dimensional view.

The analysis outlined above is based on the assumption that the Kikuchi lines are due to coherent secondary scattering of primarily elastically scattered electrons, though elsewhere the view is held that the primary scattering is incoherent. It would seem difficult to account for the definition of the black and white Kikuchi lines and their distance apart, however, in terms of coherent secondary scattering of incoherent electrons. Furthermore, we would expect Kikuchi lines lying in the region near the intersection of the plane of the crystal face with the screen to be broader than elsewhere, if the first scattering were inelastic; and no such effect is to be observed in any of the fluorite patterns. Finally, in obtaining the pattern, Fig. 17, a small bar magnet was interposed between the crystal and photographic plate. Comparison with the corresponding normal pattern, Fig. 14, shows that the distortion is considerable. Nevertheless, the distorted pattern reveals no blurring of the Kikuchi lines or other pattern features, although it seems reasonable to suppose that a chromatic range equivalent to 200 volts in the 50 KV. electrons could hardly have escaped detection. We therefore conclude that, apart from the general background, the patterns are wholly due to coherent scattering.

Electron Diffraction by Transmission through Single Crystals.—We have seen that in the diffraction of a beam grazing a crystal face two of the three Laue conditions are partially relaxed. In transmission through a single crystal, however, two Laue conditions must be rigid, because two atom rows of lengths limited only by the width of the wave front are normal, or nearly so, to the beam; and to what extent, if any, the third Laue condition is relaxed will depend upon the thickness of the crystal, *i.e.*, upon the length of the atom rows in the beam direction, and this will in effect be limited by the penetrating power of the electrons.

The pattern, Fig. 18, was obtained by transmission through a thin mica single crystal, the beam being normal, or nearly so, to the cleavage plane, and hence nearly parallel to the *c* axis. The spots reproduce the pseudo-hexagonal symmetry of the corresponding projection of the lattice points in the mica crystal so perfectly as to suggest either that the pattern is a real cross-grating effect or that the crystal was either deformed or possessed mosaic structure. The first alternative postulates relaxation of the third Laue condition; the second, on the other hand, supposes that the crystal exhibits just that degree of imperfection which would be necessary for the diffracted rays to be true three-dimensional effects. Apart from its unlikelihood, this second alternative can be easily disproved. Thus the mica crystal could be rocked through at least $\pm 4^\circ$, *i.e.*, an angle greater than any of the normal critical Bragg angles of incidence, about any axis in the cleavage plane without appreciably affecting the geometry of the spot pattern, and any change in spot

intensity occurred symmetrically about the axis of rotation except where spots coincided with the diffuse Laue rings faintly visible in the pattern. Clearly the conditions were such that only two Laue conditions had to be rigidly fulfilled, although in fact the specimen was a three-dimensional crystal. From the breadth of the zero order maximum, from which it can be calculated that the crystal was about 150 Å. thick, it follows that the third Laue condition was relaxed for those atom rows parallel, or nearly so, to the beam. With progressively thicker mica specimens the transmission patterns, Figs. 19, 20 and 21, exhibit the influence of the increasing rigidity of the third Laue condition. Thus, in Fig. 19, spots lying on the Laue rings are much the brightest, and in Figs. 20 and 21 all other spots are practically extinguished. Furthermore, definition decreases, the general background of scattering increases, secondary scattering giving rise to Kikuchi lines becomes more and more pronounced and, in the case of Fig. 21, the main beam is approaching extinction, although the third Laue condition was still not sufficiently rigid to eliminate all except purely three-dimensional diffraction effects.

The tolerance in the angle of incidence increases with decreasing thickness. Thus, the pattern, Fig. 22, was obtained from mica which was probably much less than 100 Å. thick. Spots equidistant from the undeflected spot are approximately equally intense; moreover, there is an approximately uniform radial decrease in intensity. The pattern reveals no evidence of a third Laue effect. Inclining the *c* axis to either side of the beam about an axis in the cleavage plane and parallel to a row of pattern spots led to a symmetrical reduction in spot intensity about the axis of rotation; furthermore, the hexagonal symmetry became impaired as the angle of tilt was increased beyond about 5°, whilst the positions and intensities of the spots on the axial row remained unchanged. The effect of such excessive tilt upon a mica transmission pattern is clearly seen in Fig. 23; in this case, however, the hexagonal symmetry has completely disappeared, owing to the fact that the crystal was rotated about an axis, the projection of which lay between two spot rows.

A single crystal face can be etched or abraded so as to leave fragments which, though integral with the crystal, project above the surface.²⁵ With the beam at grazing incidence, such specimens yield typical cross-grating patterns, as in Fig. 24, thus showing that in this case the "reflection" is really a transmission effect.

Electron Diffraction by Polycrystalline Materials.—A polycrystalline specimen in which the crystals are pointing in every conceivable direction is equivalent to a single crystal rotating freely. If the mica crystal giving the spot pattern, Fig. 18, had been rotated during exposure, a pattern of sharp rings would have been obtained. Rotation of the crystal yielding the pattern, Fig. 21, however, would give rise to a picture consisting of little other than diffuse background. Thus, the electron diffraction ring patterns, where the rings stand out so clearly from background must be, unlike X-ray powder patterns, really two-dimensional effects. A similar conclusion has been reached by Thomson¹⁸ who calculated that for 30 KV. electrons the mean free path for ionisation in a solid is of the order of 4×10^{-8} cms., and has pointed out that crystals with atom rows of this length in the beam direction will act mainly as two-dimensional gratings.*

* With X-rays, owing to the fact that the diffraction effects are three-dimensional, the angles of incidence are critical to within seconds or at most a few minutes. In the case of the diffraction of electrons by a polycrystalline film, this tolerance is,

In determining the lattice plane spacings from electron diffraction patterns, Bragg's relationship, $2d \sin \theta = n\lambda$, may be used. Owing to the two-dimensional nature of the effects, however, θ is no longer the critical angle of incidence upon a reflecting plane, but is to be regarded as half the scattering angle; and d is the spacing between atom rows upon a plane normal to the beam, provided the third Laue condition is only relaxed for atom rows which do not deviate by more than 5° from the beam direction. Thus d will have the same value as the spacing between planes parallel, or nearly so, to the beam, and the pattern dimensions can therefore be interpreted in accordance with established X-ray methods. Combining Bragg's relationship with the camera and pattern dimensions we have, in view of the small scattering angles involved,

$$d_{hkl} = \lambda L / R_{hkl},$$

where L is the camera length, d_{hkl} the effective spacing, and R_{hkl} the radius of the corresponding ring.

Theoretically, ring-width or spot-diameter cannot be less than the beam cross-section. We have, however, obtained patterns in which the rings or spots were much finer. This suggests that the effective specimen area in such cases is less than the beam cross-section, and proof of this view was afforded by the following experiment. By scraping the edge of a sheet of mica with a sharp needle, a minute specimen giving a spot pattern was obtained; the sheet to which it adhered was too thick to transmit. The beam diameter could be varied between 0.1 and 2 mm. without appreciably affecting either the definition or size of the spots, other than that due to the undeflected beam. Thus an abnormal ring and spot narrowing can be ascribed to a reduction of the effective specimen area to less than the beam cross-section by surrounding masses of opaque material. On the other hand, it is easy to see that an excessive tolerance in the angle of incidence due to extreme crystal thinness may lead to an abnormal broadening of certain rings. As in X-ray diffraction, the breadth of the diffracted rays enables an estimate to be made of the size of the grating, *i.e.*, of the crystal; but in so doing, these abnormal broadening and narrowing effects should be taken into consideration.

As pointed out above, Thomson¹⁵ has shown that "reflection" at grazing incidence by a polycrystalline film is in effect transmission; one half of the pattern, however, is cut off by the shadow of the substrate.

Orientation in Polycrystalline Specimens.—Intensity measurements play an important rôle in X-ray structure analysis; in electron diffraction, however, the cross-grating nature of the patterns introduces uncertainties which are further increased by the fact that the crystals in a thin film are usually more or less orientated.

The crystals in a polycrystalline aggregate are said to be in random

however, in general at least $\pm 4^\circ$, and sometimes much more; accordingly there will be a corresponding increase in the intensity of the effects; and this circumstance, in conjunction with the approximately 10^7 times more intense nuclear interaction of electrons as compared with the extra-nuclear electronic scattering of X-rays accounts for the brilliance of the electron diffraction effects on the fluorescent screen. In addition, it may be noted that, with collimation by a single anode diaphragm and magnetic focussing, a beam carrying $10\mu\text{A}$. at 60 KV. can be obtained with an input of only 60 watts to the discharge tube. One of the great advantages of electron diffraction in structure analysis lies in the visibility of the patterns on the fluorescent screen and in the short exposures, generally less than half a second, required for their recording on plates of normal emulsion types.

array when the same type of plane may be found pointing in every direction; in diffraction this is equivalent to a single crystal exercising to the full all rotational degrees of freedom. If a given zone axis is pointing in the same direction in each crystal, then the aggregate is equivalent to a single crystal rotating about that axis, and the crystals are said to have a common direction of orientation. Finally, if the crystals possess in addition another direction in common, we have the equivalent of a single crystal devoid of motion.³

A random specimen, no matter what the direction of the electron beam, will give a ring pattern in which every possible diffraction will appear (Fig. 25). When the crystals have one common direction of orientation, however, the appearance of the pattern will depend upon the angle between this direction and that of the beam. Thus, when these two directions are at right-angles, a cross-grating pattern consisting of a fuller array of spots than could be yielded by a stationary crystal will be obtained. If both directions coincide, the pattern will consist of rings; their number, however, will be less than that afforded by the random specimen, because only spacings of planes parallel, or nearly so, to the electron beam are recorded in the pattern (Fig. 26). Owing to tolerance in the angle of incidence, combined with imperfect orientation, the patterns obtained at intermediate positions, instead of consisting of spots only, will be more or less arced, according to the angle of inclination (Fig. 27). If the orientation is not perfect but such that, for example, the particular zone axial directions are evenly distributed within certain limits about the preferred direction of orientation, then the pattern will consist either of arcs or complete rings, according to the angle made with the beam. As a rule, the crystals in thin polycrystalline films and surfaces exhibit a pronounced tendency towards orientation, particularly in one common direction; they do so in such a manner that certain planes in all the crystals are more or less parallel to the plane of the film or substrate. Thus orientation of this type must always give rise to arcing in "reflection" patterns (Figs. 28, 29 and 70), whilst in transmission through a plane specimen normal to the beam the absence of certain rings and the abnormal intensities of others, together with arcing as a result of inclining the film to the beam, testify to the presence of orientation, and enable its nature to be determined (Figs. 52 and 53). Hence, although absence of arcing in a transmission pattern does not justify the assumption that the crystals are random, a pattern of uniform rings obtained by "reflection" from a plane specimen is almost certain evidence of lack of orientation (Figs. 55 and 57). If the crystals are orientated with respect to a substrate of large curvature, for example zinc oxide crystals orientated with their hexagon bases in contact with the surface of the wire of a fine-meshed gauze, the diffraction pattern may fail to reveal any trace of orientation, even when the general plane of the specimen is steeply inclined to the beam (Fig. 25). A random array of a few large crystals gives rise to a pattern in which the rings are broken up into irregularly distributed spots (Fig. 43). In the case of Fig. 29 the relatively large crystals show a tendency to orientate with (100) faces parallel to the matrix.

In what follows, it will be convenient to define the first degree of orientation in terms of that set of planes which is parallel to the specimen plane. When two directions of orientation are present, a statement to this effect, together with the nature of the first degree of orientation, completely defines the conditions. Thus in Fig. 42 there are two degrees of orientation, the first being (100) or cube face.

"Extra" Rings and Bands.—So-called "extra" or forbidden rings have been observed from time to time in electron diffraction patterns, and their origin has been attributed to half-order diffractions or impurities. The intensity of the "extra" rings is usually feeble compared with that of the normal pattern rings, and cases in which more than one such ring have occurred in a single pattern have been rare.

In April, 1934, in conjunction with Mr. C. H. Sun, we began to study by electron diffraction the structure of electro-deposited metal films. From the first it was a striking feature of nearly all the patterns obtained from such films that they were not only more or less rich in "extra" rings, but also often exhibited one or more remarkable circular bands. Such composite patterns consisting of normal and "extra" rings and bands have now been obtained with electro-deposited films of platinum, gold, silver, cobalt, nickel, chromium, iron and tin (Figs. 59, 60, 62, 65, 67, 69, 72, 77, 84 and 85). The mean radii of the principal "extra" rings lying within the 200 ring and obtained with silver electrodeposited on cadmium, gold on copper, and with platinum on nickel are given in Table III.

TABLE III.

Metal.	Number of Patterns.	Mean Radii of "Extra" Rings.			Normal (111) Ring.		"Extra" Rings.		Normal (200) Ring.
Ag	6	0.99	1.10	1.40	Band				
					1.65	1.73	1.76	1.78	2.00
Au	8	0.99	1.09	1.36	Band		1.76	1.78	2.00
					1.64	1.74			
Pt	6	0.99	1.10	1.40	1.67	1.73	1.76	1.79	2.00

At first we attempted to account for these "extra" rings on the supposition that the electrons leave the crystals, which have throughout (110) orientation, partly through (110) and partly through (120) crystal faces, and that the atoms in these faces behave as pure two-dimensional cross-gratings.²⁶ Thus (110) exit planes normal to the beam, in acting as two-dimensional gratings of grating constants a and $a/\sqrt{2}$ in directions at right angles to each other, would give rings of radii 1.00, 1.41, 1.73 and 2.00 on the above scale with either undiffracted or once-scattered coherent electrons. Similarly, with a (120) exit face, remembering that the orientation is (110), we have as constituent line gratings, a normal to the

beam, and $\sqrt{\frac{3}{2}}a$ at $73^\circ 13'$ to the beam, the angle in projection between the line gratings being $64^\circ 50'$; and this cross-grating leads to rings of radii 0.98, 1.11, 1.12, 1.73, 1.76, 1.78, 1.95 and 2.00. The agreement with the "extra" rings actually observed is close, and by postulating suitable crystal planes as exit faces, it was possible to explain on these lines the origin of all "extra" rings obtained up to that time. More recently, however, we have obtained transmission patterns in which the normal rings were strongly arced (Fig. 42), whilst the "extra" rings were continuous, and *vice versa* (Fig. 63), and these new facts negative the

above-outlined two-dimensional view of their origin. Experimental results just to hand and set forth below now prove conclusively that the "extra" rings and bands owe their origin to the interstitial entry of gas into the crystal lattice. Thus, after heating a gold foil specimen giving a pattern of normal rings alone (Fig. 40), to 300° for 20 minutes in air, a pattern was obtained containing, in addition to the normal rings, "extra" rings corresponding to the following spacings: 4.81, 4.00, 2.79, 1.83, 1.61 and 1.49 Å., fitting a close-packed hexagonal structure, $a = 5.58$ Å. and $c/a = 1.28$ (Fig. 41). On heating this specimen in the evacuated diffraction camera by radiation from a red-hot tungsten filament, the "extra" rings gradually lost in intensity, and after 1 hours' heating had disappeared completely, leaving only the normal rings. Another fresh gold foil heated under similar conditions, but *in vacuo*, showed no change other than a slight increase in crystal size and orientation. Similar experiments with aluminium, silver and chromium foils heated in air gave patterns containing not only "extra" rings, but also prominent bands which could be eliminated by heating *in vacuo*. If the heating in contact with air or oxygen were sufficiently prolonged at 500° C., both silver and gold films gave rise to patterns consisting solely of "extra" rings (Fig. 73). In this case, however, although further heating *in vacuo* led to the extinction of the "extra" rings, the normal pattern rings failed to reappear, and the specimen gave no coherent pattern. It is clear, therefore, that the bands and "extra" rings are due to the entry of gas into the lattice. We are not dealing now with a case of definite compound formation, because the bands must be regarded as evidence of the *gradual* expansion of the lattice with entry of gas, but rather with a solid solution of gas in the superficial layers of the metal. Furthermore, in the case of aluminium, the "extra" rings formed by heating in air can be eliminated by heating, slowly *in vacuo*, but very rapidly in contact with hydrogen.

In the case of the entry of oxygen into a cubic lattice, it appears from the dimensions of the bands and "extra" rings that the oxygen atoms enter the lattice across a cube edge, to take up the body-centred site in a face-centred cubic structure and a face-centred position in a body-centred cube.

Whilst the subject of "extra" rings and bands will be discussed more fully elsewhere, it may be remarked here that it is a surprising, though none the less welcome, discovery that the diffraction of high-speed electrons is able to afford an insight into the absorption of gases by metals, and is thus destined in all probability to play an important rôle in the elucidation of the mechanism of heterogeneous catalysis, and in the study of the occlusion of gases by electrodeposited metals.

"Extinction" Rings.—Recently we have obtained a random mica pattern containing a single well-defined *black* ring in a pattern of otherwise white rings (Fig. 35). Whilst no definite interpretation can be put forward at the moment, this black ring is probably due to an extinction effect similar to that postulated in the case of the black Kikuchi lines. Rings of somewhat similar appearance have also been occasionally observed in the case of diffraction patterns containing bands and extra rings. In such cases, however, the dark ring appears to be due to the near approach of two bands, rather than to an actual extinction effect (Fig. 87).

Some Applications to the Study of Metal Films and Surfaces.

In pattern, Fig. 40, obtained from thinned commercial gold foil, the rings are complete and their relative intensity distribution (e.g., 111 and 200 rings are of approximately equal intensity) suggests that the crystals are random. Usually, however, the crystals in rolled or beaten metal foils display at least one degree of orientation, which in the case of face-centred cubic structures is generally cube face (Fig. 41), and often there are two imperfect degrees of orientation more or less approaching the single crystal state (Fig. 42). Suitable heating in air not only increases both the crystal size and orientation, but also brings into prominence "extra" rings (Figs. 41 and 42) or bands (Fig. 45) or both (Fig. 47). If the heat treatment be sufficiently intense, the normal ring pattern may be entirely displaced by one of "extra" rings alone (Fig. 73).

It is well-known that in regard to crystal growth some metals respond more readily to heat treatment than others; thus, whilst gold is rather sluggish, aluminium readily forms single crystals, as is shown by the series of patterns, Figs. 43, 44, 45, 46 and 47. Fig. 43 was obtained from a thinned commercial aluminium foil; quickly drawing through the hot gases of a Bunsen flame increased both size and orientation of the crystals, as indicated by the arcs and the many little spots irregularly distributed along the arcs (Fig. 44). After further heating, it will be seen from Fig. 45 that one single crystal of cube-face orientation had been formed, although many random crystals were still present. In the case of Fig. 46, two well-developed single crystals occurred; one in cube-face, the other approaching octahedral orientation; and later these coalesced to form a single crystal in cube-face orientation (Fig. 47). Finally, with more intense heating, the specimen burnt to form a random array of Al_2O_3 crystals, though a small part of the aluminium single crystal still survived (Fig. 48).

Although heat favours orientation, it is by no means necessary. Orientation is often obtained when crystals are formed on a cool substrate. Thus, electrodeposited face-centred cubic metals generally display (110) orientation, whilst those of the body-centred cubic type prefer to deposit in (111) orientation; and in the case of the metals enumerated in Table I. this tendency is well pronounced, even with such low current densities as 0.1 amps./ $\text{dc}.\text{cm}^2$, and a bath at room temperature. Similarly, gold, silver and platinum films deposited from colloidal solutions prepared by Faraday's arc dispersion method or by Svedberg's H.F. modification generally display (110) orientation (Figs. 82 and 83), though silver sometimes exhibits (111) orientations (Figs. 26 and 27). Again, in the case of zinc flashed on to a cool massive disc of copper, a screen being in such a position as to shield the receiver from direct radiation from the filament, the crystals often show a tendency to take up (001) orientation.^{6, 23} In the case of platinum films cathodically sputtered on to glass or quartz, factors such as the nature and pressure of the gas, and the rate of sputtering often exert a controlling influence which outweighs any thermal effect²⁰ (Fig. 92).

Early observations by G. P. Thomson²⁵ showed that a substrate could impose certain of its characteristics upon a deposited film. For example, he found that silver electrodeposited on an etched (100) face of a copper single crystal followed the orientation of the copper, but with normal silver spacings. We have sputtered gold, under conditions favourable to the production of a random film, on to a glass receiver,

one-half of which was covered by sputtered platinum in (111) orientation, and then found that the gold over the platinum had taken up a similar orientation, but was random on the glass.

A striking example of the influence of an active substrate is afforded by the effect of a platinum substrate upon the structure of a superimposed thin aluminium film, the crystals of which are forced into a face-centred tetragonal structure with basal dimensions similar to those of the platinum, but with a major axis equal to the length of side of unit cube of normal aluminium.⁶ Such basal-plane pseudomorphism is the two-dimensional analogue of the pseudomorphism so well known to crystallographers.

In many cases the Beilby²⁷ polish layer on metals has the remarkable property, not shared by the corresponding crystalline surface, of dissolving crystalline metal films deposited thereon.²³ Thus, at room temperature zinc crystals dissolve rapidly in polished copper, and somewhat less readily in polished mild steel surfaces; but are insoluble in either of these surfaces after the Beilby layer has been removed by etching. With sufficient deposition, the Beilby layer becomes saturated, whereupon further deposited layers retain their crystal structure indefinitely. Similar effects have been observed with Zn, Sn, Pb and Ag flashed on to Cu, mild steel, Pb, Au and Zn surfaces; and with Cd and Li films condensed on a copper polish layer. More recently, we found that whilst 30 seconds electro-deposition at 0.1 amp./dc.² sufficed to form a permanent crystalline zinc layer on crystalline copper, 3 minutes were necessary if polished copper served as basis metal.

In addition to exerting the above-outlined orientating, pseudomorphic and solvent effects, an active substrate may also effect the crystal size, particularly in the case of electrodeposits. Thus we have found that chromium deposited on copper gives smaller crystals and consequently broader ringed patterns than on nickel, iron, tin or bismuth, although the experimental conditions such as bath temperature and current density were otherwise unchanged (Figs. 76, 77, 78, 79, 80 and 81). The substrate also appears in certain cases to exert a profound effect upon the occlusion of gas by an electrodeposited film, as is shown by the various "extra" ring and band systems in Figs. 76, 77, 79 and 80.

Matrices also exert pseudomorphic and orientating effects. Thus, the layer of oxide formed when a clean zinc surface is exposed to oxygen at room temperature is basally pseudomorphic with the underlying zinc, and is highly orientated in that it forms in a sense a continuation of the zinc lattice.³ The basal dimensions of the pseudomorphic zinc oxide are similar to those of zinc, and the contraction in volume this entails in the oxide lattice is nearly balanced by an increase in the length of the major axis, the volume of the unit cell of pseudomorphic zinc oxide being only about 6 per cent. less than that of the unit cell of normal zinc oxide.⁶ On heating, the pseudomorphic modification is converted to smaller crystals of the normal oxide, thus exposing the zinc surface afresh, whereupon a further layer of pseudomorphic oxide is formed.

The nickel selenide, Figs. 28 and 29, formed by passing selenium vapour over heated nickel does not crystallise in the usual hexagonal form, but has a cubic structure analogous to that of pyrites. The composition of this selenide is therefore probably NiSe_2 , instead of NiSe . Both patterns show (100) orientation, but the crystals were much larger in the specimen giving Fig. 29.

When a polished copper surface is degreased with trichlorethylene

vapour, it loses the power of absorbing crystalline metallic films deposited upon it, and we have found that this is due to the formation of an invisible layer of crystalline cuprous chloride in (111) orientation (Fig. 75).

The transmission and reflection patterns, Figs. 52, 53 and 54, obtained from very thin layers formed by the evaporation of a solution of colloidal graphite ("aquadag") show that the crystal flakes are highly orientated with the cleavage-slip plane parallel to the support. In films prepared from a suspension of graphite of similar particle size, however, the flakes are randomly disposed, as is shown by Fig. 55. These facts readily explain certain well-known differences in the properties of such graphite films; thus, those prepared from the colloid are better lubricants and more easily "wetted" by oil, have greater covering power (opacity), more constant and uniform electrical resistance and show greater powers of adhesion than those formed from a graphite suspension.

Smooth surfaces of cast-iron of the quality used in internal combustion engine cylinders, after light rubbing with No. 0000 emery paper yield the characteristic, more or less orientated graphite pattern, Fig. 56, usually without any trace of iron rings. Mild steel similarly treated gives the ordinary body-centred cubic α -iron pattern (Fig. 57). Thus, in the case of cast-iron, friction brings up occluded graphite, and spreads it over the surface where it acts as a lubricating layer protecting the iron from abrasion.

The orientated graphite patterns obtained at grazing incidence may be likened to a reflection pattern from the face of a single crystal rotating in the azimuthal plane. It seems that the dimensions of the graphite flakes are such that they are too thick to transmit in directions parallel, or nearly so, to the hexagon planes, but are sufficiently thin to diffract in directions steeply inclined to these planes. This view is born out, not only by the appearance of the patterns from orientated graphite, but also by the fact that oox type rings are always diffuse in both transmission and "reflection" patterns obtained from random specimens. Mr. A. L. Williams, working in this laboratory, has found that a random graphite specimen gave a pattern similar to Fig. 54 after compression in a vice, the graphite film being covered for this purpose by a thick tin foil. This result strongly supports the view outlined above, according to which the colloidal graphite flakes are thin (about 100 Å., or less) in the direction normal to the basal planes, but far too thick to transmit electrons in directions coinciding, or nearly so, with the basal planes.

Recently we have examined the working surfaces of four aeroplane engine cylinder sleeves which Mr. H. T. Tizard and Dr. D. R. Pye kindly placed at our disposal. Two of these sleeves were honed and ready for service; the other two had been run-in, the one for 40 hours, the other for 140 hours. After removal of the protective grease layer by washing with petrol-ether, the external and internal surfaces of the virgin sleeves both yielded patterns characteristic of a random crystal structure and in which α -Fe rings were prominent. The run-in surfaces, on the other hand, after degreasing gave the halo pattern typical of the Beilby layer. The thickness of this layer was such that several abrasions with No. 000 emery paper were necessary before the halos gave way to the normal well-defined ring pattern of the virgin sleeve surfaces. Thus it seems that the process of running-in an internal combustion engine consists in the formation on the working surfaces of an amorphous Beilby layer of considerable depth.

APPENDIX.

Direction cosines (λ, μ, ν) **of the normal to the net plane** (h, k, l) **with respect to three orthogonal axes** $OX_3Y_3Z_3$.

Take the b axis along OY_3 and the a axis in the plane OX_3Y_3 on the positive side of X_3 .

Triclinic system.—Axes a, b, c ; angles α, β, γ between bc, ca, ab .

$$\lambda = \left(\frac{h}{a} + \frac{k \cos \gamma}{b} \right) \cdot d / \sin \gamma,$$

$$\mu = k \cdot d / b,$$

$$\nu = [abl \sin^2 \gamma + bch(\cos \alpha \cos \gamma - \cos \beta) + ack(\cos \beta \cos \gamma - \cos \alpha)] \cdot d / V \sin \gamma;$$

where $d = 1 / \sqrt{\Sigma a^2 b^2 l^2 \sin^2 \gamma + \Sigma 2a^2 bckl(\cos \beta \cos \gamma - \cos \alpha)}$,

$$V = abc \cdot \sqrt{1 - \cos^2 \alpha - \cos^2 \beta - \cos^2 \gamma + 2 \cos \alpha \cos \beta \cos \gamma}$$

(d is the net plane spacing and V is the volume of the unit cell).

Rhombohedral system.—Axes $a = b = c$; angles $\alpha = \beta = \gamma \neq 90^\circ$.

$$\lambda = (h + k \cos \alpha) \cdot d / a \sin \alpha,$$

$$\mu = k \cdot d / a,$$

$$\nu = [l \sin^2 \alpha + (h + k) \cdot (\cos^2 \alpha - \cos \alpha)] \cdot a^2 d / V \sin \alpha;$$

where $d = 1 / a^2 \cdot \sqrt{\Sigma l^2 \sin^2 \alpha + \Sigma 2kl(\cos^2 \alpha - \cos \alpha)}$,

$$V = a^3 \cdot \sqrt{1 - 3 \cos^2 \alpha + 2 \cos^3 \alpha}.$$

Monoclinic system.—Axes a, b, c ; angles $\alpha = 90^\circ$; $\beta; \gamma = 90^\circ$.

$$\lambda = h \cdot d / a,$$

$$\mu = k \cdot d / b,$$

$$\nu = \left(\frac{l}{c} - \frac{h \cos \beta}{a} \right) \cdot d / \sin \beta;$$

where $d = 1 / \sqrt{\left(\frac{h^2}{a^2} + \frac{l^2}{c^2} - \frac{2hl \cos \beta}{ac} \right) \sin^2 \beta + \frac{k^2}{b^2}}$.

Hexagonal system.—Axes $a = b, c$; angles $\alpha = \beta = 90^\circ, \gamma = 120^\circ$.

$$\lambda = (2h + k) \cdot d / a \sqrt{3},$$

$$\mu = k \cdot d / a,$$

$$\nu = l \cdot d / c;$$

where $d = 1 / \sqrt{(h^2 + k^2 + hk) \cdot 4/3a^2 + l^2/c^2}$.

Rhombic system.—Axes a, b, c ; angles $\alpha = \beta = \gamma = 90^\circ$.

$$\lambda = h \cdot d / a; \mu = k \cdot d / b; \nu = l \cdot d / c;$$

where $d = 1 / \sqrt{\Sigma h^2 / a^2}$.

Tetragonal system.—Axes $a = b \neq c$; angles $\alpha = \beta = \gamma = 90^\circ$.

$$\lambda = h \cdot d / a; \mu = k \cdot d / a; \nu = l \cdot d / c;$$

where $d = 1 / \sqrt{(h^2 + k^2) / a^2 + l^2 / c^2}$.

Cubic system.—Axes $a = b = c$; angles $\alpha = \beta = \gamma = 90^\circ$.

$$\lambda = h \cdot d/a; \mu = k \cdot d/a; \nu = l \cdot d/a,$$

where $d = a/\sqrt{\Sigma h^2}$.

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INNER POTENTIALS OF CRYSTALS AND THE ELECTRON DIFFRACTION.

By W. E. LASCHKAREW.

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§ 1. Introduction.

Systematic deviations from Bragg's law for electron diffraction may be explained, as is well known, by the existence inside the crystal of an electrical potential ϕ , exceeding of the surrounding space.

Assuming this potential constant, we can determine its magnitude from a modified form of Bragg's equation which takes into account both change of wave-length of the electron inside the crystal and its refraction at the crystal-vacuum boundary.

For the special case of symmetrical reflection from the plane parallel crystal surfaces, the usual Bragg relation

$$2a \sin \theta = n\lambda = \frac{\sqrt{150}}{\sqrt{V}} n \quad . \quad . \quad . \quad (1)$$

may be transformed into :

$$\sqrt{V \sin^2 \theta + \phi} = \frac{\sqrt{150}}{2a} n \quad . \quad . \quad . \quad (2)$$

where

λ = wave-length in Ångströms,
 V = electron energy in volts,
 θ = "Bragg" angle,
 n = reflection order,
 a = grating parameter in Å.
 ϕ = inner potential in volts.

Of course, the potential inside the crystal is actually not constant but is a periodic function of the three-space co-ordinates. The potential ϕ determined from equation (2) gives some mean value of the actual potential, which we may call the "effective" or internal potential.

Let us consider first the relationship existing between this effective potential and the actual potential $U(x, y, z)$. This relationship may be most easily shown by considering a one-dimensional crystal for which the potential depends only on a single co-ordinate Z , being constant in planes parallel to the crystal surface (Laschkarew^{1, 2}).

For the electron wave, such a crystal appears as a medium with an index of refraction which is also a periodic function of Z only,

$$\mu = \sqrt{1 + \frac{U(Z)}{V}} \quad . \quad . \quad . \quad (3)$$

Considering the optical path difference for the electron waves which are scattered from consecutive crystal layers separated by distances corresponding to the period a , we arrive at an equation somewhat more complicated than equation (2), namely :

$$\frac{1}{a} \int_0^a \sqrt{V \sin^2 \theta + U(z)} dz = \frac{\sqrt{150}}{2a} n \quad . \quad . \quad (4)$$

Equating relations (2) and (4), we obtain equation (5) for the determination of the effective potential Φ ,

$$\frac{1}{a} \int_0^a \sqrt{V \sin^2 \theta + U(z)} dz = \sqrt{V \sin^2 \theta + \Phi} \quad (5)$$

Consideration of this equation leads to several important conclusions.

For high orders of reflection, *i.e.*, when $V \sin^2 \theta$ is sufficiently large to satisfy the inequality

$$V \sin^2 \theta + W_0 \gg |W_0 - U(Z)| \quad (6)$$

where

$$W_0 = \frac{1}{a} \int_0^a U(Z) dZ \quad (7)$$

the effective potential is then given by

$$\Phi = \frac{1}{a} \int_0^a U(Z) dZ = W_0 \quad (8)$$

that is, it equals the mean grating potential.

On the other hand, for low orders of reflection

$$\Phi < W_0 \quad (9)$$

With increasing order, Φ increases, approaching W_0 asymptotically, *i.e.*,

$$\lim_{n \rightarrow \infty} \Phi_n = W_0 \quad (8')$$

The mode of increase of Φ is determined by the characteristics of the potential $U(Z)$.

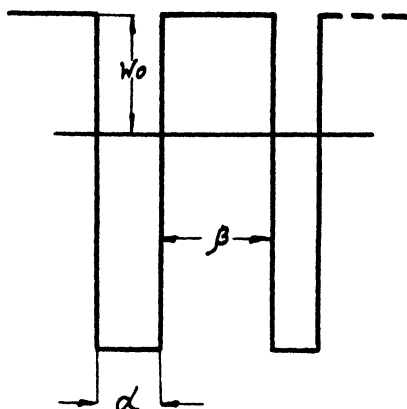


FIG. 1.

$\frac{\Phi}{W_0}$ (as a function of $\frac{V \sin^2 \theta}{W_0}$ (see Fig. 2) for the form of potential shown in Fig. 1), has been calculated for various values of α (the grating parameter a is equal to unity).

From our previous considerations, it follows that the internal potential is in no way connected with the presence or absence in the crystal of conduction electrons, and therefore in principle cannot be used to determine the number of the latter ones.

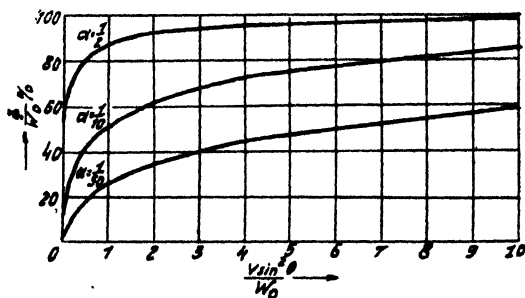


FIG. 2.

§ 2 Effective Potential and the Diffraction of Fast Electrons.

For the determination of the effective potential from experimental data we shall first examine results obtained by the diffraction of fast electrons. (We shall omit the description of the generally-known technique.)

Comparative data obtained for different substances by various authors are given in the following table:—

The values tabulated give a constant effective potential which may be ascribed to reflections of medium and high orders.

In the case of reflections of very low orders, first Yamaguti,³ and later Kikuchi and Nakagawa,⁴ discovered that the effective potential has lower values than it has for high

TABLE I.

Substance.	Φ .	Observer.
MoS ₂	17.1	Yamaguti ³
MoS ₂	17	Kikuchi and Nakagawa ⁴
NaCl	10	Thomson ⁶
NaCl	10	Raether ⁶
NaCl	7.7	Yamaguti ⁷
ZnS	7.6	Raether ⁶
ZnS	2.6	Dixit ⁸
ZnS	12.7	Yamaguti ³
ZnS	12.2	Kikuchi and Nakagawa ⁴
Calcite	12.4	Yamaguti ⁷
C (graphite)	11.48	Yamaguti ³
C (graphite)	10.7	Jenkins ⁹
Mica	10.6	Yamaguti ¹⁰

orders, in agreement with the theory given above. Fig. 3, reproduced from the paper by Kikuchi and Nakagawa,⁴ illustrates the results obtained for MoS₂ by themselves as well as Yamaguti. Their curve is very similar to the theoretical curves (Fig. 2).

Discrepancies in the numerical values obtained by different authors for many substances, such as for instance ZnS, may be explained by difficulties, wrong ordering of diffraction maxima.

Actually this ordering is a matter of solving a system of equations of type (2). However, the number of equations, which is equal to the

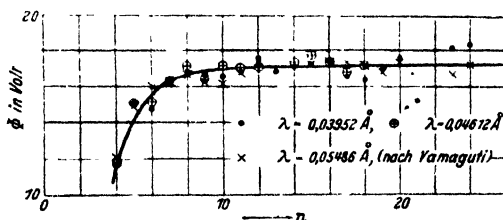


FIG. 3.

number of observed reflections, is less than the number of unknowns (orders of reflection + effective potentials Φ). Besides, the variation of Φ for low orders has been considered only in the last work of Yamaguti³ and Kikuchi and Nakagawa.⁴

The possibility of finding the effective potential and of avoiding the difficulties in ordering is considered in § 7.

§ 3 Mean Grating Potential.

As we have seen, the general considerations of § 1 give an explanation of the increase of the effective potential with the order of the reflection. Now we shall try to confirm the reality of the coincidence of the asymptotic value of the effective potential with the mean grating potential. The mean potential of the crystal may be calculated either on the basis of general wave mechanical considerations, or from X-ray grating reflection intensities.

The first method, based on approximate calculations by Hartree,

has been used by Bethe¹¹ for calculating the mean potential in nickel. However the assumption that a grating atom has the same electron density distribution as has an isolated atom (this assumption lies at the basis of these calculations) is not acceptable for the outer and essentially valence electrons which alone practically determine the mean grating potential.

The second method is based on the fact that X-ray scattering factors (F_{ik0}) give a unique determination of the electron density distribution in the crystal. As is known from X-ray theory these are the coefficients in the expansion of the electron density function in a triple Fourier series :

$$\rho(w) = \sum_{-\infty}^{+\infty} \sum_{-\infty}^{+\infty} \sum_{-\infty}^{+\infty} F_{ik0} e^{i(f_{ik0}, w)} \quad . \quad . \quad . \quad (10)$$

Knowing the positions of the nuclei in the grating as well as the electron density distribution, it is possible to calculate the potential at each point, as well as the mean potential of the entire grating. This calculation, involving a summation of the very slowly converging series (10), became feasible only after the development of a new method (Laschkarew,¹² Laschkarew and Tschaban¹³), which we will give briefly. We replace the real atoms in the grating by fictitious ones satisfying the following conditions :

1. The fictitious (or as we term it, "equivalent") atom possesses spherical symmetry.
2. The grating built up by the following method has the same scattering factors as the real one. The centres of equivalent atoms are situated in the points of real grating. The density of electrons and electric fields of the separate equivalent atoms overlap one another.

We have shown also a simple method of determining the equivalent atom.^{12, 13} With the equivalent atom known, and using it to build up the grating, we can easily find the potential at any point of the grating by adding the electric fields due to neighbouring equivalent atoms. Besides this, we can also calculate the mean grating potential.

The accuracy of the proposed method is limited by the precision of the X-ray atomic factor measurements. Using the most precise data available in the literature, it is possible to speak of average potential calculations with an accuracy of one volt, especially in the case of dielectrics. In the case of metals, the distribution of the densities of the conduction electrons cannot be observed with sufficient accuracy from X-ray analysis.

This method was used in calculating the potential distribution, as well as the mean potential, for a series of gratings. (Li, Al, NaCl, C-diamond.) The mean potential $W_0 = 8.4V$ found for NaCl appeared to be in excellent agreement with the asymptotic value of the effective potential given by Yamaguti ($7.7V$) and in satisfactory agreement with the data of Thomson and Raether ($10V$).

Comparison of $\lim_{n \rightarrow \infty} \Phi_n$ and W_0 was not made for other substances because of a lack of reliable X-ray data.

Figs. 4 and 5 show the potential distribution in gratings of NaCl (001 planes) and Li (011 planes). The mean grating potential was taken as zero (dotted curve).

Fig. 6 shows the potential variation along the line joining adjacent atoms of sodium and chlorine in NaCl. Fig. 7 gives a similar curve for

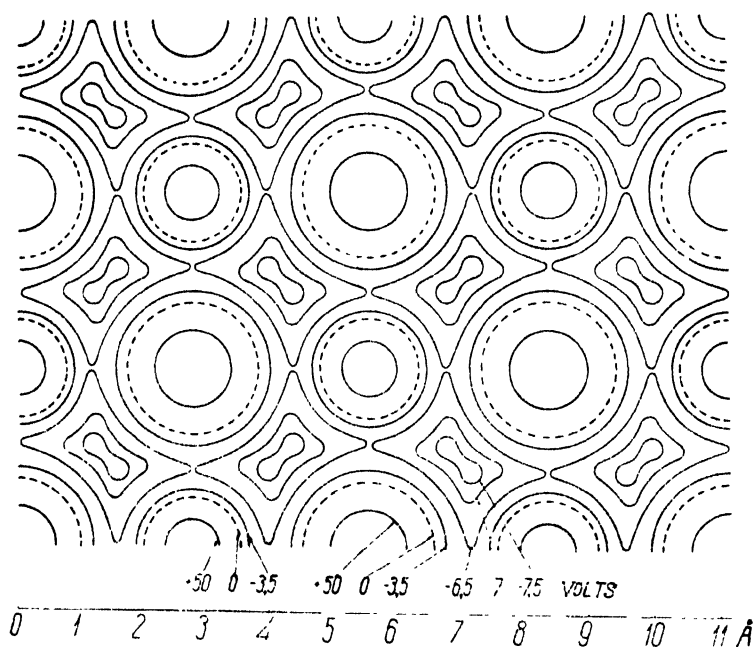


FIG. 4.

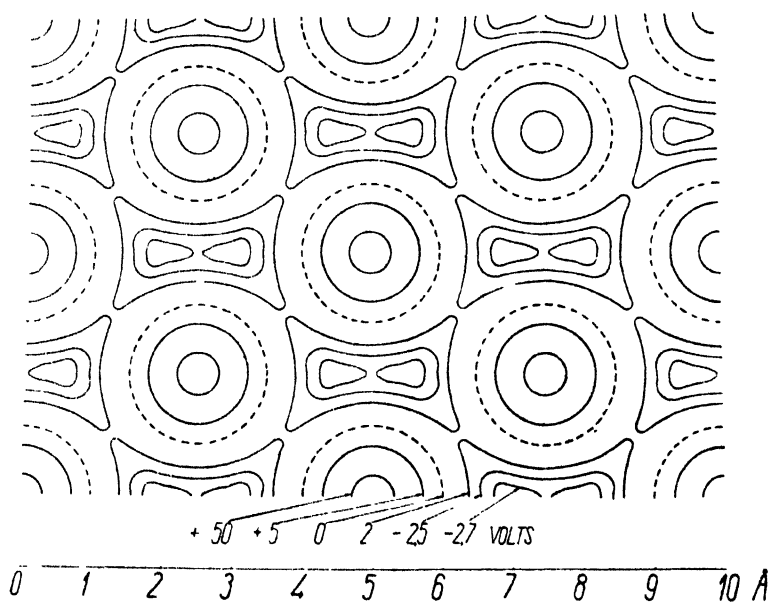


FIG. 5.

lithium. The mean potential was again taken as zero. The solid straight line at the top of the drawing shows the electrical potential of the outside space. The dotted line is lower than the upper one by the magnitude of the work function which is determined from the Richardson effect or from the red wave-length limit of the photoeffect.

Neglecting the image force, this dotted line gives the total energy of an electron at the highest energy level in the crystal.

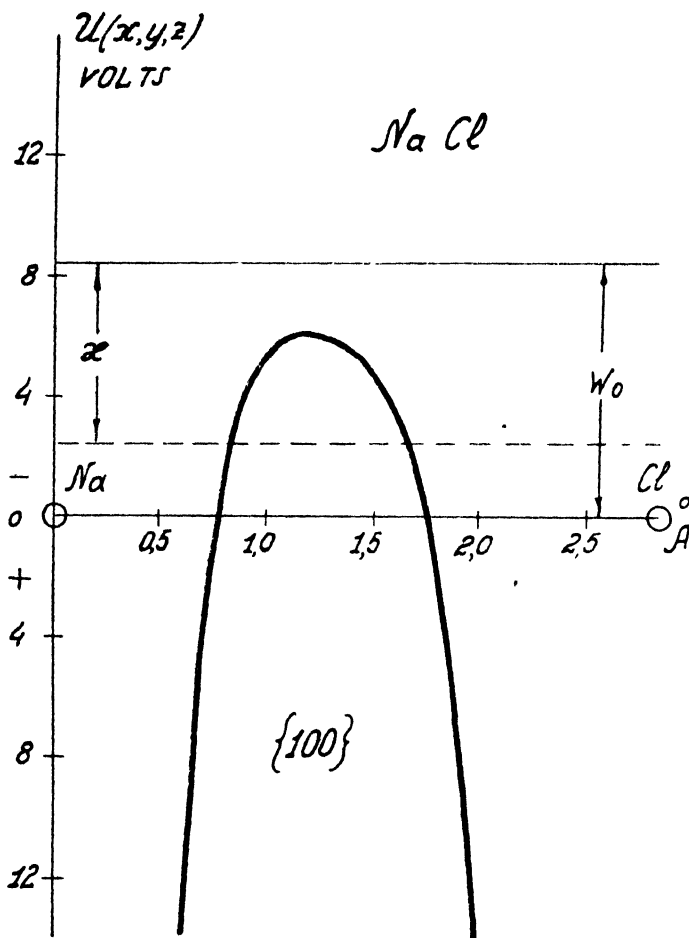


FIG. 6.

In the case of dielectrics this assumption is nearly true. In the case of metals this dotted line is the low limit of the possible position of the electron level.

From Figs. 6 and 7 it may be seen that the level of the electron with the greatest total energy lies lower than the potential hump between the grating atoms in the case of the typical dielectric NaCl; while in the case of the metal Li it lies higher. This condition, but not the magnitude of the mean potential, appears to be the characteristic difference between metal and dielectric.

§ 4. Effective Potential and Slow Electron Diffraction.

The determination of the effective potential using diffraction of slow electrons meets with many difficulties, and the results obtained are often difficult to interpret.

Table II. gives the variation limits (in volts) of the effective potential determined with single crystals of several metals.

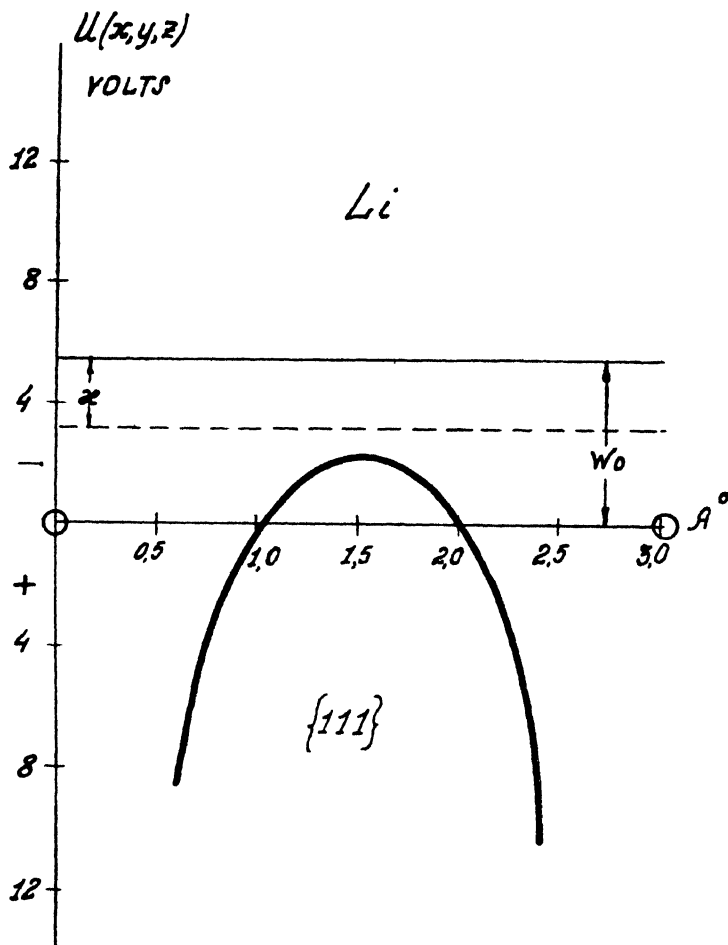


FIG. 7.

Only in the case of nickel is there an observed grouping of the values of Φ near the average; in the case of the others, Φ has random values with only a slight tendency towards large values for high incident electron speeds.

Difficulties of a fundamental character, which one encounters in the study of the diffraction of slow electrons, arise due to:

1. Ordering of the maxima.
2. Determining the location of the maxima.

TABLE II.

Substance Φ .	From	To	Difference.	Observer.
Ni	- 21	+ 48	69	Davisson and Germer ordering according to Bethe. ¹¹
Cu	+ 5	+ 31	26	Farnsworth ¹⁴
Cu	+ 7	+ 35	28	Ehrenberg ¹⁶
Ag	- 3.7	+ 24.1	27.8	Farnsworth ¹⁴
Au	- 1.5	+ 36.1	37.6	Farnsworth ¹⁵

The difficulties in ordering are connected with the presence of many diffraction maxima which cannot be identified with those observed with X-rays. Those maxima which are identically the same as with X-rays, we shall term *regular* in distinction from the *irregular* or additional maxima. The number of irregular maxima (according to Farnsworth's data) may be several times greater than the regular ones. Obviously, the determination of the effective potential should be preceded by a careful investigation of the nature of the observed maxima.

Comparing the results of various authors, we arrive at the conclusion that the additional maxima may have the following origins :

- (a) Surface grating.
- (b) Regular reflection with effective potential $\Phi = 0$.

Davisson and Germer¹⁷ considered that these maxima are caused by interference from echelon on the crystal surface. The both above indicated types of maximum are usually very weak, which corresponds to the conditions causing them.

(c) Selective variation of the crystal surface reflection factors in the region of very slow electrons (observed and studied by Laschkarew and Kuzmin¹⁸ for the case of graphite).

- (d) "Prohibited" maxima.
- (e) Fine structure.

§ 5. Prohibited Maxima.

By "prohibited" maxima we understand those which although corresponding to a grating with the same parameters as the one investigated, require, however, either combinations of orders not permitted by structure factors, or else require half-orders (so-called "half" maxima). Maxima of this nature represent a characteristic property of electron diffraction, and have been observed by practically all workers in this field.

Attempts have been made, first by Davisson and Germer,^{19, 20} to explain these prohibited reflections as due to surface gas adsorption, or to gas penetration inside the grating (Rupp,²³ Thomson⁵). According to Farnsworth, the gas adsorbed on copper forms either a simple cubic grating with a parameter equal to that of the copper, or else a face-centred cubic grating having a grating parameter twice that of the copper. Farnsworth also obtained similar results for silver and gold.

The disappearance or weakening of the prohibited maxima which has been observed in several cases with lengthy out-gassing of the sample seems to substantiate the above views.

Kohler and Laue²¹ attempted to explain the "half" maxima, observed by Laschkarew, Bärengarten and Kuzmin²² in the case of graphite, by supposing that the atoms of carbon in alternate layers (0001) have somewhat different atomic factor values. However, such an explanation is connected with quantitative difficulties. Letting F_1 and F_2 be the different atomic factor values, we find for the intensity relation between prohibited and regular reflections a value of the order of:

$$\left(\frac{F_1 - F_2}{F_1 + F_2}\right)^2 \quad . \quad . \quad . \quad . \quad (11)$$

Even for $F_1 = 2F_2$, which is quite improbable, this relation equals $1/9$, while experimentally, it is near unity and sometimes even larger. Similar quantitative difficulties are encountered also in the explanation of the half-maxima as due to a change in the scattering properties of the planes caused by the absorbed gas arranging in the grating in layers with the double parameter.

The explanation of the half-maxima which assumes a special adsorbed gas layer structure does not appear to us to be finally proved, since we are aware of cases where such an explanation certainly does not apply.

Let us consider the important observations made by Raether⁶ on the diffraction of fast electrons by the (001) planes of a pyrite (FeS_2) single-crystal. If the electron beam is located exactly in azimuth 001, all the prohibited reflections with odd index l [of type $(002n + 1)$] are present, with no difference in intensity from that of the regular reflections. For a slight azimuth change, all the prohibited maxima disappear. Raether expressed the opinion that the odd orders in his experiments were due to double reflection inside the crystal.

We think it would be correct to search for an explanation of the effects observed by Raether on the basis of some kind of special characteristics of the electron diffraction itself. There are other arguments in favour of the above, such as the fact that for many other cases the explanation of half maxima by gaseous adsorption is very improbable. These arguments are based on the equality of the effective potential and the temperature effect (§ 7), for both half and regular maxima (as shown by us in the case of graphite²²). The equality of the effective potential for both kinds of the maxima was calculated by us on the basis of data given by Farnsworth for symmetrical reflections from (001) copper (see § 6).

§ 6. Fine Structure and Location of the Maxima.

By fine structure we understand small maxima, discovered by Farnsworth, which are especially defined near the main maxima and strongly affect the latter. Fig. 8 which is reproduced from the work of Farnsworth (with additions by us) illustrates this.

Curves A, B, C show the reflections of electron from the plane (001) of copper at azimuth (110) for three angles of incidence: 8° , 10° , 12° from the normal. The solid line curves are given by Farnsworth. The numbers over the maxima have been put in by us to indicate the orders of the reflections from the (001) face corresponding to these maxima. The odd orders of maxima are prohibited. An explanation of the fine structure may be found by the following considerations based on the dynamic theory of scattering.

Let us assume, for example, that we are investigating the symmetrical

reflection of electrons from planes parallel to the crystal surfaces. Keeping the angle of incidence constant and changing the speed of the incident electrons we should obtain, for several particular voltages, besides the reflection under investigation, new diffracted reflections from other grating planes. The intensities of these new reflections will be partially at the expense of a weakening of the symmetrical reflection. Therefore, there will appear on the curve of the investigated symmetrical reflection, depressions ("shades") at those voltages for which intensive reflections arise from other planes.

Depending on its position, this "shading" may cause a splitting of

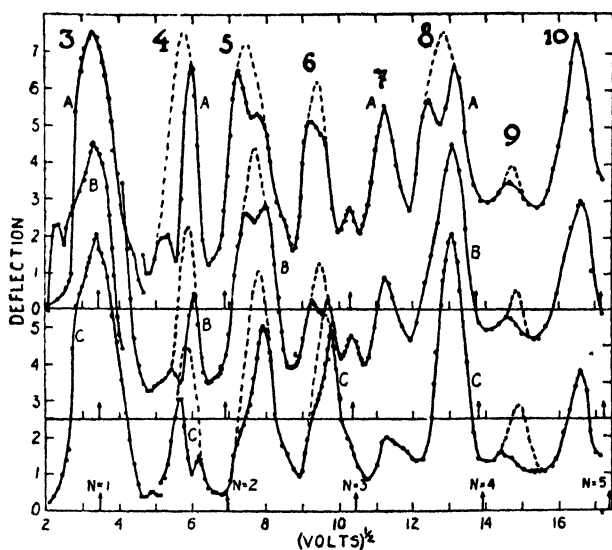


FIG. 8.

a maximum on the curve of the symmetrical reflection or a shifting of the maximum in one or the other direction.

Let us consider the case of electrons incident on a cubic grating bounded by the face (001) of the cube (xy). Let us assume that the electron beam forms an angle θ with the Z -

axis and lies in an azimuth forming an angle ψ with the x -axis. Let us assume further that the inner potential of the crystal is constant and equal to Φ . Then the location of the "shading" caused by diffraction from the plane (ikl) can be determined (in volts) from the following equation:

$$l \cos \theta \sqrt{V + \frac{\Phi}{\cos \theta}} + (i \cos \psi + k \sin \psi) \sin \theta \sqrt{V} = \frac{\sqrt{150}}{2a} (i^2 + k^2 + l^2). \quad (12)$$

Equation (12) shows that the location of the "shading" is strongly dependent on the ray inclination (θ) and on the azimuth (ψ), which was also determined by Farnsworth. In particular cases, for small θ (corresponding to Fig. 8) the "shading" shift with voltage, and for increase of the angle θ , has a sign opposite to that of the expression:

$$i \cos \psi + k \sin \psi.$$

The "shading" shift may be clearly seen on Fig. 8. The dotted line shows the hypothetical form which, in our opinion, the maximum should have had if it were not distorted by the "shading" effect. The

dotted curve, moreover, shows to what extent the deformation of the maximum may displace its peak and thereby cause an incorrect determination of the effective potential.

Determining, for the case analysed, the corrected locations of the maxima and also determining the orders, we have found for the effective potentials of copper, values having a regular increase with increase of reflection order (see Fig. 9). Only the first prohibited maximum ($n = 3$) falls outside the smooth curve for Φ . It is possible that this maximum (at 11 volts) belongs to type (c) § 4. Fig. 9 shows that the asymptotic value of Φ for copper exceeds 25 volts. We consider this result quite

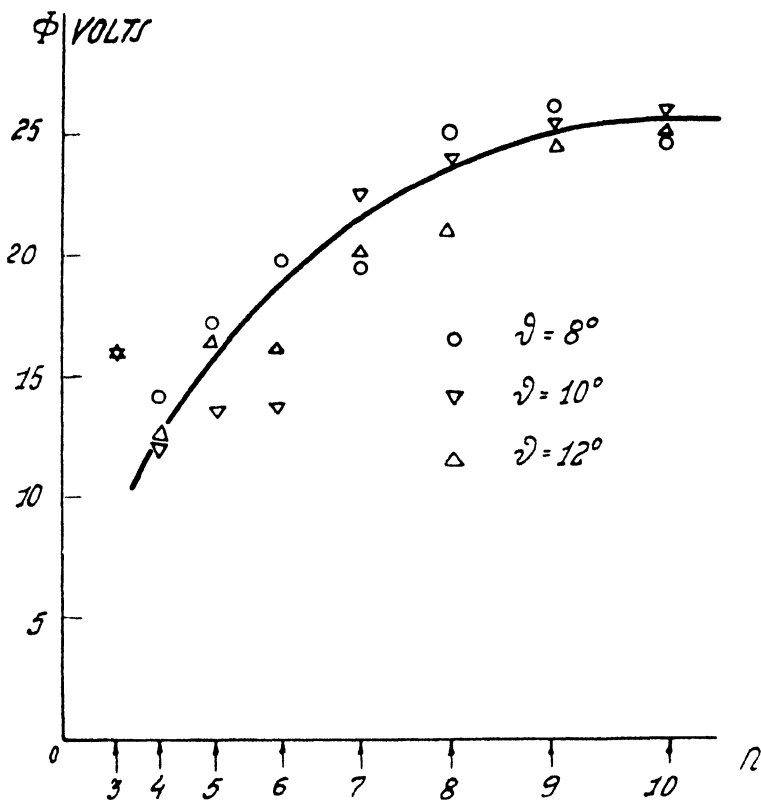


FIG. 9.

probable and corresponding to that value of the inner potential (25-30 volts) which we calculated on the basis of data given by Rusterholtz²⁴ for the atomic factor of copper.

The ordering of the "shadings" is a more complicated problem than the ordering of the maxima, as the possibilities in the first case are much greater (potentials Φ and all possible combinations of i, k, l). The number of combinations of i, k, l should be especially large if attention is given also to all of the prohibited reflections, which must be done regardless of the origin of the latter. The question of the resolution of the fine structure is connected with the as yet untouched question of intensities in the case of diffraction of slow electrons. It is quite clear that

the fine structure for various substances having similar gratings (Cu, Ag, Au) may differ strongly in complexity (because of differences of potential variation inside the grating), as has been observed by Farnsworth. For the case given in Fig. 8, the fine structure maxima "4" and "5" may be ordered as (022) and (133) with an effective potential of 25-30 volts. The shift with angle occurs correctly both as to sign and magnitude.

The determination of the effective potential is obviously connected with the location of the maxima undistorted by the fine structure. The elimination of this distortion is obtained automatically with a proper arrangement of the experiments. Thus, fine structure is not observed in oriented fine crystalline aggregate (Rupp²⁸); for in that case the direction of the normal is retained with respect to a definite plane

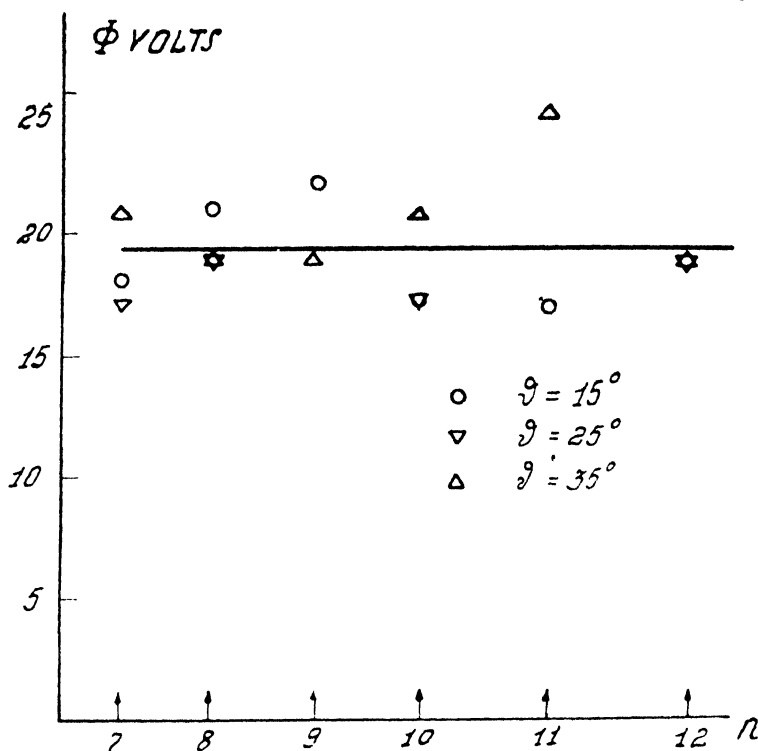


FIG. 10.

(i.e., angle θ), while the azimuth of ϕ can assume any value thus entirely damping out the fine structure which is highly dependent on the azimuth (see equation 11). In the case of graphite we did not observe fine structure in many samples. In the latter cases it was possible to show, using X-rays, that the sample consisted of mono-crystal cells with parallel (0001) planes, but having various azimuths. This allowed us to easily assign for graphite a constant effective potential equal to 18-20 V.

We cannot at present say whether the difference of this value from that obtained by other workers with fast electrons (11 volts) is due only to sample differences or to peculiarities of the diffraction of slow electrons. Fig. 10 shows the value of ϕ obtained for graphite from different reflection orders for different angles θ (odd orders prohibited).

Using a single crystal, it should be possible in principle to eliminate the fine structure by a fast rotating of the crystal about the normal to the investigated plane (parallel to the sample surface).

§ 7. Temperature Effect.

The determination of the inner potential is equivalent to measuring (λ_i) the length of the electron wave inside the crystal. As we have seen above, such measurements based on deviations from the Bragg relation, that is on comparison of λ_i with the grating parameter, are connected with serious ordering difficulties. A study of the temperature effect may allow measurement of the effective potential by comparison of λ_i with the amplitude of the heat oscillations of the grating, using a method not connected with ordering. The essentials of this method will be briefly presented.

The temperature coefficient of Debye for X-rays has the form

$$I_T = I_{T_0} e^{-\frac{\sin^2 \theta}{\lambda^2} \phi(T, T_0)} \quad (13)$$

where I_T and I_{T_0} are the diffraction maximum intensities for temperatures T and T_0 , θ is the Bragg angle, λ is the wave-length, and $\phi(T, T_0)$ is the function of Debye, which depends on the temperature and on the properties of the grating.

The correctness of equation (13) for the diffraction of fast electrons has been shown theoretically by Pisarenko.²⁵ For slow electrons the validity of this equation has been experimentally investigated by Laschkarew and Kuzmin¹⁸ in the case of graphite.

From the derivation of (13) it follows that the values of θ and λ should be those for the inside of the grating. Denoting these by θ_i and λ_i we can, considering the effect of the refraction of the electron waves, receive the values of θ and λ for the outside of the crystal by means of the transformation:

$$\frac{\sin^2 \theta_i}{\lambda_i^2} = \frac{\sin^2 \theta + \frac{\Phi}{V}}{\lambda^2} = \frac{\sin^2 \theta}{150} \left(V + \frac{\Phi}{\sin^2 \theta} \right) \quad (14)$$

in which we assume the potential Φ constant. From equations (13) and (14) it follows that:

$$I_T = I_{T_0} e^{-\frac{\sin^2 \theta}{150} \cdot \phi(T, T_0) \cdot \left(V + \frac{\Phi}{\sin^2 \theta} \right)} \quad (15)$$

For graphite in the temperature range of 230-560° C., we have obtained the following empirical expression for the temperature effect

$$I_T = I_{T_0} e^{-q(T - T_0)(V + \psi)} \quad (16)$$

in which q and ψ are constants.

By comparing formula (15) and (16) with the experimental law (16) we determined the effective potential to be effectively constant and equal to:

$$\Phi = \psi \sin^2 \theta = 18 \text{ volts.}$$

Afterwards the ordering of the maxima for graphite could be uniquely carried out and proved to correspond to that proposed earlier. The latter fact shows that in the case of graphite the magnitude of Φ obtained from the temperature effect coincides with the effective potential used in explaining deviations from the Bragg relation.

Comparing our observed value of the temperature effect with that known from X-ray diffraction, we have found that the oscillations of the atoms in the first grating layers (from which the diffraction of slow electrons arises) do not differ appreciably from the oscillations of atoms in the deeper layers.

It must be remarked that the temperature effect should be an especially sensitive indicator for showing the nature of the "prohibited" maxima, because its value is to a high degree dependent on the masses of the scattering centres, and on their relations with the grating. Because of this, the maxima formed by mixtures (with gases for example) should be distinguished by different temperature characteristics. In the case of graphite, we did not observe such a difference between the prohibited and allowed maxima. One of the maxima (8 volts), which earlier was considered by us as regular, showed somewhat too small a temperature effect, which first drew our attention to its special nature (see § 4).

§ 8. Conclusion.

In this paper we review the present state of the question of the inner, or more exactly the "effective" potential in relation to electron diffraction.

By considering of a simplified model of a uni-dimensional grating, we have shown that the effective potential is not a constant, but increases with the order of the diffracted reflection, asymptotically approaching the average grating potential.

Taking as example fast electrons, we show that the effective potential really follows the expected variation.

In § 3 we consider a new method for calculating the potential distribution in the grating and the mean grating potential from X-ray data. Using NaCl as example, the mean potential coincides with the asymptotic value found from diffraction of fast electrons. The independence of the effective potential value from the presence or absence of free electrons in the grating is specially noticed.

In § 4 we consider those special difficulties which arise in the determination of the effective potential when using diffraction of slow electrons, *viz.*:

(a) Determination of the orders of reflection, due to the presence of numerous additional maxima.

(b) Determination of the location of the maxima due to the close relation of their form with the "fine structure."

We consider the origin of the additional maxima, particularly the "prohibited" (§ 5) and the fine structure (§ 6) maxima. Arguments are adduced to show that the "prohibited" maxima (in particular the half-maxima) are not caused by gaseous adsorption, but are connected with fundamental characteristics of electron diffraction. Analysis of the origin of the "fine" structure indicated the possibility of its elimination, thus excluding several especially important sources of error in the determination of the effective potential.

In § 7 we consider the temperature factor in relation to electron diffraction, and show that with its use it is possible to arrive at unique reflection orders, and an unique determination of the effective potential. The possibility of applying the temperature factor to the investigation of the origin of the "prohibited" maxima is shown. The considerations of § 7 have been checked in the case of graphite.

The characteristics of electron diffraction which we have sought to understand herein may be, we think, derived, without doubt, from wave mechanics through further development of the fundamental investigations of Bethe¹¹ and Morse.¹⁶ Difficulties encountered in attempts to apply this method to the problems of electron diffraction have a purely mathematical character; as yet not overcome.

In conclusion, we wish to express our thanks to Professor P. I. Lukirsky for his valuable help in discussing the problems which are considered in this paper, and also to thank Mr. N. L. Pisarenko for his valuable suggestions, connected with the theory of electron diffraction.

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THE THICKNESS OF THE AMORPHOUS LAYER ON POLISHED METALS.

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Introduction.

It is proposed to devote the first part of this paper to a summary of the investigations into the nature of polish, and to contrast the various conclusions which have been drawn from the experimental results.

Up to the last few years, research in the subject necessarily had been almost entirely confined to optical methods. With the recent development of the electron diffraction technique, however, so admirably suited to investigation of surface structure, the enquiry into the nature of polish has received fresh impetus.

It will be convenient, therefore, first to deal with the earlier investigations using the microscope, and secondly the more recent work employing electron diffraction methods.

In the first years of this century Sir George Beilby¹ published the results of a comprehensive series of experiments carried out with a number of polished surfaces. The general method that he used was to note, by means of the microscope, the various changes produced in the nature of a surface during the polishing process, and then to observe the converse set of changes as the polish was removed by etching the surface.

As a result of this work, Beilby came to the general conclusions that for all types of surface "sufficiently homogeneous to be polished at all, the fundamental principles on which polishing depends are absolutely identical," and that "the polished surface on a solid is as truly due to the presence of a surface tension skin as is the surface of a liquid." His view is that while grinding merely flattens the surface, polishing causes the surface to flow, and that the final surface is covered by a "vitreous" or amorphous layer. He likens the polished surface to a super-cooled liquid, and visualises the structure as "an instantaneous photograph of the molecules in the liquid state."

Beilby explains the hardening of metals by cold working as being due to the formation of the amorphous modification at the internal slip surfaces.

Criticism of the theory seems to have been levelled chiefly at this last conclusion, rather than at the work connected with polish, although in the latter connection mention should be made of Barker's² experiments on the crystallisation of sodium nitrate on a polished calcite surface. He found that the sodium nitrate crystals orientated themselves with respect to the crystallographic directions of the underlying single crystal of calcite. It is difficult to draw any definite conclusions from this as Beilby himself found that such a parallel growth also occurs when sodium nitrate is allowed to crystallise on an unpolished cleavage face of calcite coated with a very thin layer of polycrystalline calcium oxalate or carbonate.

Benedicks³ opposed the amorphous theory on the grounds that Beilby's results could be better explained in other ways. In particular, he considers hardening by mechanical working to be the result of "poly-synthetic twinning." This explanation, however, does not appear to hold generally, as recent work on single crystals shows that mechanical working is not necessarily associated with twinning. For example, according to Gough,⁴ single crystals of cubic face-centred metals do not twin readily by cold working; yet hardening occurs in the process. Thus, although there is no definite proof of the existence of the amorphous modification at the slip surfaces of distorted metal crystals, this hypothesis seems preferable to Benedicks' theory.

Tammann⁵ follows Benedicks in considering the amorphous theory unnecessary.

Adam⁶ accepts Beilby's view that the polished surface is in an amorphous state, but does not consider that the surface is actually liquified in the process of polishing. He considers it more probable that the "moving polisher adheres to the surface atoms and drags them about on the surface," thus producing an amorphous layer.

¹ Beilby, *Aggregation and Flow of Solids*, London, 1921.

² Barker, *J. Chem. Soc.*, 1906, **89**, 1120.

³ Benedicks, *Rev. Met.*, 1922, **19**, 505; *Metallographic Researches*, New York, 1926.

⁴ Gough, *Aeronautical Research Committee*, Rep. and Mem., 1930, 1432.

⁵ Tammann, *A Text-book of Metallography*, New York, 1925, 1432.

⁶ Adam, *The Physics and Chemistry of Surfaces*, Oxford, 1930.

The short summary given above outlines the conclusions as to the nature of the polish layer that can be inferred from experiments with the microscope. The rather more detailed evidence afforded by electron diffraction methods will now be considered.

French⁷ appears to have been the first to use electron diffraction in this connection. He confined his investigations to metals, but used both single and polycrystalline surfaces. He found, in general, that, when a polycrystalline metal surface is polished, the characteristic ring pattern becomes blurred. The diffuseness of the pattern increases as the polishing process is pushed further, until finally only two broad diffraction maxima are obtained. He interpreted these facts as indicating that when a metal surface is ground and polished the crystal size is gradually reduced until finally there is a random arrangement of the atoms as in a liquid—that is, as predicted by Beilby: or alternatively, if any crystal structure is present in the polished surface the crystals cannot contain more than two or three unit cells. On the assumption that the surface is, in fact, amorphous French was able to estimate the closest distance of approach of the atoms for the metals concerned. His values are in good agreement with X-ray measurements.

Analogous results were obtained from a polished single crystal of chromium.

It was suggested by Professor Kirchner⁸ that the gradual broadening of the rings might be attributable only to a gradual flattening of the surface, and not to the formation of an amorphous layer. Germer⁹ also advanced the opinion that French's results might be explained by a levelling out of the surface. This view was discounted by French on the ground that the final two smudgy rings should in this case be displaced and distorted by the refraction effect at the metal surface. No such effect, however, is observed.

The work of Darbyshire and Dixit¹⁰ confirmed and amplified the investigations of French. By using metals which were not face-centred they were led to the conclusion that the diffuse polish rings cannot be due to very small crystals but are, in fact, due to an amorphous layer. In certain cases the interatomic distance in the layer was found to be smaller than that observed in X-ray work. They also examined polished specimens of iron pyrites and galena, but here they found nothing in support of the amorphous layer theory. It is interesting to note that the amorphous layer was observed on polished selenium and silicon surfaces.

Raether¹¹ carried out a series of comprehensive experiments on the changes produced in the surfaces of metals and insulators by cold working. He concurs with French's view that an amorphous layer is produced by polishing a metal surface. In the case of polished surfaces of ionic crystals no evidence pointing to the existence of an amorphous layer was obtained.

Finally the work of Finch, Quarrell and Roebuck¹² indicates that the amorphous layer is present in the case of polished metal surfaces.

It will be seen from the foregoing that there is definite evidence that the amorphous layer exists on polished metal surfaces. Other explanations do not appear to fit the experimental results so well. The reasons

⁷ French, *Proc. Roy. Soc.*, 1933, A 140, 637.

⁸ Kirchner, *Nature*, 1932, 129, 545.

⁹ Germer, *Physic. Rev.*, 1933, 43, 724.

¹⁰ Darbyshire and Dixit, *Phil. Mag.*, 1933, 108, 961.

¹¹ Raether, *Z. Physik*, 1933, 86, 82.

¹² Finch, Quarrell and Roebuck, *Proc. Roy. Soc.*, 1934, A 145, 676.

for rejecting the other interpretations have recently been discussed by Professor Thomson.¹³

Thus it may be concluded that the Beilby layer exists on polished metal surfaces, but no evidence is at present forthcoming from electron diffraction experiments to support the view that it exists on polished surfaces of ionic crystals.

Beilby estimated the thickness of a layer formed by polishing a cleavage face of calcite, by etching the surface with very dilute acid, and observing under the microscope the various changes in appearance so produced. No other determinations of the thickness of the polish layer appear to have been made, although Raether suggests tentatively a figure of 10^{-6} to 10^{-7} cms. for metals.

General Considerations.

It is the object of these experiments to determine the thickness of the amorphous layer in the case of a polycrystalline metal surface.

1. Choice of Material.—In choosing a metal to work with it is essential that the metal decided upon shall not oxidise readily and that it can be polished with reasonable ease. It was therefore decided to use gold.

2. Choice of Method.—Considered from a general point of view, the obvious way of measuring the thickness of the layer is to polish the specimen and then find out how much material has to be removed before the layer can no longer be detected.

Electron diffraction methods can differentiate between the presence and absence of the amorphous layer, so it remains to find a method of removing the layer and estimating the mass of metal taken off in the process.

Etching by chemical means suggests itself immediately, but this idea was abandoned as the etching process does not give uniform removal. Electrolytic removal is another possibility.

Finally a method originally proposed by Dr. L. C. Martin was employed. This consists in making the polished metal the cathode in a spluttering chamber. The spluttering action gradually removes the metal surface, and the mass rate of spluttering can be determined by a subsidiary experiment.

The method has the great advantage that the rate of removal is controllable over a wide range by varying the conditions of operation of the spluttering vessel. It seems reasonable to suppose the removal is uniform as a rough calculation indicates that the number of gold atoms removed under the conditions described below, is of the same order as the number of incident positive ions.

Apparatus Used.

Spluttering Chamber.—In designing the spluttering apparatus to ensure uniform spluttering, it was necessary to arrange for a symmetrical arrangement of the electrodes. Further, it was necessary that the cathode should be readily accessible.

The apparatus used consisted of a glass bulb, with the positive electrode sealed into the upper end. At the other end of the bulb was a ground joint, through which connection to the pumping system was made.

The cathode consisted of an aluminium disc, into the centre of which

¹³ Thomson, *Phil. Mag.*, 1934, 18, 640.

the gold specimen fitted so that the surface under test was flush with the aluminium surface. This arrangement of the specimen in the cathode ensured that the spluttering should be as uniform over the surface as possible.

The pressure in the bulb was controlled by a needle valve leak.

A test discharge tube of approximately the same dimensions as the spluttering chamber was sealed in the pump lead to the latter.

The high tension supply for the spluttering apparatus was obtained from a small induction coil, one side of the secondary of which was earthed. The output was valve rectified and smoothed by a 0.02 mf. condenser. The voltage across the tube was measured by an electrostatic voltmeter, and the current by a milliammeter connected in series with the earth return from the anode.

Experimental Procedure.

1. Polishing of Specimen.—The specimen consisted of a rectangular block of pure polycrystalline gold of 1 centimetre square cross-section

The surface was ground smooth by light rubbing on 00, and 000 emery paper, using benzene as lubricant. The final grinding was by 0000 emery paper. The specimen was rubbed in one direction till the surface showed a series of fine scratches all in the direction of rubbing. It was then turned through a right-angle and rubbed across these scratches until they were all obliterated, and the fine surface cuts were again all in the direction of rubbing. This method was employed by French. It was sometimes necessary to repeat the procedure as frequently a fairly deep scratch developed during the final grinding.

The specimen was then washed to remove traces of emery adhering to the surface.

The polishing process consisted of rubbing the specimen lightly on clean chamois leather: the specimen was rotated at frequent intervals, so that there was no definite polishing direction.

After washing in alcohol—(other organic liquids were tried)—the surface was ready for investigation.

2. Preliminary Examination of Surface.—At this stage the surface structure of the specimen was investigated by electron diffraction, using apparatus similar to that described by Professor G. P. Thomson.¹⁴ This preliminary testing of the surface was necessary in order to make sure that the amorphous layer was actually present. It was readily detectable by the characteristic two diffuse rings described by French and others.

3. Removal of Polished Layer by Spluttering.—The surface was removed step by step, by spluttering under standardised conditions for definite time intervals.

Owing to the short spluttering periods involved, it was necessary to arrange for preadjustment of conditions before spluttering. This was achieved by means of the test discharge tube.

Preliminary experiments showed that over the range 2.4–2.8 kv. and a spluttering current of 0.5–0.6 m.amp, there was no great change in the rate of spluttering, which was 0.2 mgr. per hr. within about 20 per cent. as long as the conditions were approximately constant.

4. Re-examination of Surface.—After each spluttering experiment the surface was again studied by electron diffraction.

5. Determination of Mass Rate of Spluttering.—This was determined using a microbalance. The gold was weighed before and after an extended spluttering period—usually one hour—at the standard conditions.

Results.

It was found in general that four minutes rubbing on 0000 emery paper—two minutes in each of two directions at right angles—with

¹⁴ Thomson, *Proc. Roy. Soc.*, 1930, A 128, 641.

benzene as a lubricant, and fifteen minutes subsequent polishing on clean chamois leather, was sufficient to induce the polish layer.

The time of spluttering, noted by stop-watch, was in 30 second periods. This corresponded to removing a layer of gold about 10\AA thick.

The results given refer to the above treatment.

Diffraction Patterns Obtained.

Measurement of the patterns was difficult owing to the broadness of the bands, but the following general results may be stated.

1. Before Spluttering.

The usual two diffuse rings described by previous experimenters were obtained. The mean values obtained were in good agreement with their results.

2. After Removing Various Thicknesses of Gold.

(a) 10\AA . The two diffuse rings were still present but two very faint bands appeared corresponding to the mean of the (331) (420) (422) (333), and the (531) (600) (442) spacings for gold.

(b) 20\AA to 30\AA .—Little change in pattern detectable but the bands became rather more intense.

(c) 40\AA .—At this depth the band corresponding to the (331) (420) (422) (333) planes split up into two sharper bands at the mean positions of the (331) (420) and (422) (333) spacings respectively. Similarly the outer of the two original diffuse rings disappeared and was replaced by two separate rings at the (220) and (311) (222) positions. Also a further faint diffuse ring occurred outside the (531) (600) (442) maximum. A general increase in intensity above background was again noticeable.

(d) 50\AA and over. The patterns gradually sharpened up. At about 150\AA the (111) (200) rings became resolved. At $400\text{--}500\text{\AA}$ the normal sharp gold pattern was obtained.

The results are stated generally, as they refer to the average effects observed with a number of specimens. Occasional departures from the average behaviour were observed. For example, one polished specimen still gave only the two diffuse rings after 20\AA had been removed; often orientation of the small crystals under the amorphous layer was noticeable; usually this took the form of a tendency for the (011) planes to set themselves parallel to the surface.

Discussion.

In interpreting the results the two significant facts to be borne in mind are that :—

(1) In general after removing a thickness of only 10\AA from the polished surface two extra rings appear in the diffraction pattern.

(2) The pattern gradually sharpens and becomes more intense as more and more of the surface is taken off.

In the present work the apparent glancing angle of incidence of the beam with the surface is about 1° . The actual angle of incidence might, however, be considerably greater if there are any steep projections on the surface. The fact that, in general, removing 10\AA caused two additional broad bands to appear in the pattern, suggests that there are actually no sharp lumps on the surface.

It may, therefore, be assumed that the true glancing angle of incidence at the various parts of the surface is small.

Now from work on the transmission of electrons through thin metallic films it may be concluded that an electron of about 30 kv. energy can pass through a thickness of about 500\AA before suffering an inelastic collision.

This restriction implies that for electrons incident at an angle of 1° with an absolutely flat surface, those penetrating to a depth greater than 10\AA below the surface would probably be inelastically scattered before emergence. The thickness of the layer effective in producing the pattern would, as a result, be limited to about 10\AA . In the present case it is unlikely that the surface is absolutely flat but probably consists of low lumps separated by the fine scratches produced by the final grinding. As a result of this departure from flatness the thickness of the effective layer may be increased to 20\AA or 30\AA .

It may therefore be concluded that, since after removing only 10\AA of surface a fraction of the incident electrons are elastically scattered in the substrate of very small crystals, the original thickness of the amorphous layer over most of the surface cannot be much more than 20\AA to 30\AA although it may be much thicker than this locally.

The progressive sharpening of the pattern, and the gradual emergence of the rings from the background may be explained by (a) a gradual increase in crystal size below the amorphous layer. (b) The step by step reduction in background scattering in the amorphous layer as the latter is removed.

It should be noted that at about 100\AA below the original surface the crystals are still extremely small, and a rough calculation indicates that there are about 5 or 6 atoms in each edge.

The increase in crystal size was also observed by spluttering at higher current densities, when it was found a sharp ring pattern of gold was obtained.

General Conclusion.

(1) The thickness of the Beilby layer produced as described, is about 30\AA over much of the surface.

(2) There is a gradual increase in crystal size below the polished surface.

The author would like to express his gratitude for the interest taken in the work by Professor G. P. Thomson and for his many valuable suggestions.

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THE STRUCTURE OF POLISHED METAL SURFACES.

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This paper gives a preliminary account of an investigation of the structural changes produced by polishing a metal surface. The disturbance might be expected to extend to a depth comparable with the wavelength of visible light, but previous electron diffraction work has given no information about the structure deeper than about 50 Å., because of the low penetrating power of electrons.

Previous Work.

G. P. Thomson¹ found that polished metals gave no electron diffraction pattern, and concluded that the surface was amorphous. French² carried out more detailed work. He took electron diffraction photographs of the surfaces of various metals at various stages of grinding and polishing, and concluded that the polishing produced an amorphous layer, in which the distance between neighbouring atoms was nearly constant throughout, as it is in a liquid.

Kirchner³ suggested that the absence of diffraction rings (or the presence of only two diffuse rings as found by French) could be explained without assuming that the surface was amorphous. He suggested that polishing may level the crystals in the surface until each one has a face very nearly parallel to the surface; and that refraction would then broaden the diffraction rings.

Germer⁴ made the same suggestion as Kirchner, and calculated that if a polished nickel surface (inner potential 15 volts; electron beam voltage 50 kV) consists of minute crystal faces at slightly different angles, the maximum deviation from the mean plane of the surface being $\frac{1}{2}$ degree, then the diffraction rings would be widened sufficiently to merge into one another.

The theories of Kirchner and Germer appear to the writer to be based on false assumptions, and will be referred to in the discussion.

Finch⁵ condensed a thin layer of a second metal on a polished metal surface. Electron diffraction photographs taken at short intervals afterwards showed that the condensed layer gradually vanished, until only general scattering was obtained. Finch concludes from his results that the polished surface is amorphous, and not crystalline, as suggested by Kirchner.

¹ *P.R.S.*, 1930, **128**, 641.

² *Nature*, 1932, **129**, 545.

³ *P.R.S.*, 1934, **145**, 678.

⁴ *P.R.S.*, 1933, **140**, 637.

⁵ *Physic. Rev.*, 1933, **43**, 724.

General Experimental Method.

Successive layers (of thickness from 30 to 6000 Å) were electrolytically removed from the polished surfaces of the face centred metals copper and gold, and electron diffraction photographs were taken of each new surface revealed.

The thickness of each layer removed was found either from the quantity of electricity passed during the electrolytic etching, or by colorimetric analysis of the electrolyte.

In general the polishing process has been found to produce not only a thin amorphous, or Beilby, layer, but between this and the non-oriented poly-crystalline material (which forms the body of the metal), is a much thicker layer of oriented crystals, which have 110 planes approximately parallel to the surface.

Copper.

1. Polishing Method.—The specimens were $\frac{3}{8}$ -inch lengths of $\frac{1}{2}$ -inch rod. The surface was prepared for polishing by grinding with successive grades of emery, with water, on glass laps. Three methods of polishing have been used

(a) By hand, on a pitch lap, using water and rouge (supplied by Dr. Mayer of Pforzheim). This gave a very high polish. No attempt was made to get an optical flat, as this is unnecessary for electron diffraction.

(b) Under different loads on wet rouged flannel, stretched on a rotating table.

(c) On flannel treated with a commercial liquid polish.

2. Electrolytic Etching.—The electrolyte used was sodium sulphate solution containing 2 gms. per litre. This was chosen as being unlikely to attack the copper when no current was flowing. To verify this, the Rubenic acid test for copper was used, and the electrolyte was found to dissolve less than 3 Å from polished copper in 30 seconds. This is negligible compared with the thicknesses removed electrolytically.

From the quantity of electricity passed, the mass of copper removed was calculated on the assumption that the metal was removed as cupric ions. This was checked by making a series of colorimetric determinations of the copper in the electrolyte after various known quantities of electricity had been passed. The divergence between the two methods did not exceed 25 per cent.

The amount of copper removed is most easy to visualise if expressed as a thickness, so this was calculated from the mass of copper and its density, considering the copper surface to be plane.

3. Experimental Method.—It is important to have the surface free from grease films or other deposits which might give spurious diffraction effects. The final cleaning was done by washing with acetone (redistilled over calcium chloride), and drying in an air-blast. This method has proved entirely satisfactory.

An electron diffraction photograph of the polished surface was taken. A known thickness of metal was then removed, and an electron diffraction photograph was taken of the new surface revealed. Successive etching and photographing were continued until no further changes in structure occurred. This needed between 200 Å. and 1000 Å., and at this depth the metal was poly-crystalline and non-oriented.

In agreement with previous workers, the unetched polished copper gave either no rings at all, or else two faint blurred ones. After etching, the rings were always those of cuprous oxide, not copper.

Fig. 2* is a typical photograph of the oriented layer. This was a copper specimen polished by method (a), etched to a depth of 40 Å. The crystals can be seen to be oriented with a 110 direction within about 20° of the normal

to the surface. Fig. 1* shows the same specimen at a depth of 200 Å.; the crystals are non-oriented at this depth.

At first sight, it is surprising that the orientation should be decided by the plane of the surface and have no connection with the direction of polishing. In order to check this point, a specimen, polished in one direction only, was etched, and photographed with the direction of polishing at several different azimuths with respect to the electron beam; the photographs all showed the same orientation.

There was still a possibility that the working of the copper during manufacture had affected the orientation, so experiments were carried out with sheet copper specimens instead of the rod. These gave the same orientation, namely a 110 plane in the surface.

The thicknesses of the amorphous layer and the oriented layer have been found for specimens polished by each of the three methods. They are likely to depend on the time of polishing and on the pressure used, as well as the polishing agent, but no systematic measurements of these quantities have yet been made. The figures given below must therefore not be taken as representative, but merely as the particular values which have been found in a few cases. When the final polishing was done with the medium rouge by either method (a) or (b), the amorphous layer was 20-40 Å. thick. When the commercial liquid polish was used, the amorphous layer was not always complete, and faint oriented rings were sometimes obtained before any metal had been etched away. The thickness of the oriented layer varied from 150 Å for polishing method (a) to 500 Å. for method (b).

The size of microcrystals has been estimated from the breadths of the diffraction rings, corrections of course being made for the width of the incident beam and its inhomogeneity (this is actually negligible). The results are tabulated below:—

TABLE I.

Method of Polishing	Depth	Structure.	Approx Size of Crystals	Voltage
(a)	0 Å.	Amorphous		21 kV.
	45	Oriented	170 Å.	21
	190	Non-oriented	130	15½
(b)	0	Amorphous		20 kV.
	27	Oriented	90	19
	55	"	90	17
	80	"	90	21
	130	"	90	19
	190	"	90	23
	300	"	90	21
	460	Non-oriented	130	24
(c)	0	Oriented	20	23 kV.
	70	"	70	28½
	175	"	70	22
	850	Non-oriented	100	24

The crystals in the oriented layer are not much smaller than the non-oriented crystals beneath. In the case of the specimen polished by method (a), the thickness of the oriented layer is about equal to the size of the crystals of which it is composed.

Gold.

This metal was tried next because, like copper, it has a face-centred cubic lattice but is more resistant to oxidation. Only two series of photographs have been taken.

1. Polishing Method.—The gold specimen was a $\frac{3}{8}$ -inch diameter disc, $\frac{1}{16}$ -inch thick. The metal is very soft, and to get a good polish without scratching, medium rouge on wet flannel was used.

2. Electrolytic Etching.—5 per cent. KCN solution was used, with a current density of 15 mA/cm.². The thicknesses removed were much greater than for copper; after two minutes, when about 5000 Å. should have been removed, the surface looked unmistakably etched. The KCN did not appear to dissolve the gold seriously when no current was flowing, because the surface appeared unchanged after two minutes under these conditions. It has been assumed that each atom of gold required three electrons.

Results.—Gold has a much thicker orientated layer than copper. Fig. 2 * is a photograph taken at a depth of about 10,000 Å. (= 1 μ). The orientation is accurate to about 10°.

Fig. 3 * shows the structure at a depth of about 10 μ . There is still some orientation. This is probably due to the irregularity of the etching. The diffraction pattern will be given by those parts of the surface which have been etched least. The size of the crystals is greater than 300 Å.

Discussion.

1. Kirchner⁶ suggested that the inability of a polished surface to give diffraction rings can be explained by the levelling of the faces of the microcrystals. This involves the tacit assumption that a given reflecting plane can make any angle with the face at which the electrons enter and leave. But it is well known that large crystals only develop faces of a few types, of very low Miller Indices; and it is likely that the same rule applies to microcrystals near the surface of a metal.

It has been shown in this paper that the crystals 50 Å. below the surface of copper or gold have 110 planes approximately parallel to the surface. If Kirchner's suggestion were right, the surface would then consist of 110 faces only, the orientation being correct to a few degrees.

Neglecting refraction for the moment, the diffraction pattern produced by such a surface would be similar to Figs. 2 * or 2 †, except that much shorter arcs of the rings would appear. If the orientation were accurate to an angle θ , then each arc would subtend 2θ at the centre of the pattern. The refraction becomes important because we are considering crystals which actually have a 110 face developed. It will shift each spot in a direction normal to the surface of the specimen. For 40 kV. electrons, and an inner potential of 15 volts, the maximum elongation of each spot, due to refraction, would be about 1 cm., and would occur with an orientation accurate to about 1° to 1½°. With more accurate orientation, the elongation would be less; and with less accurate orientation, most of the intensity would lie in the almost unrefracted part of the spot. Since the tangential extent of each spot increases as the orientation becomes less accurate, the area of each spot will be a maximum for an orientation accurate to say 2° or 3°, and will be of the order of 0.2 cm.². The total number of spots is about 30, and the area of the photograph about 20 cm.², so nearly all the spots would be easily separated.

⁶ *Nature*, 1932, **129**, 545.

* Plate XXIX

† Plate I.

No such spots have been observed ; therefore, the actual surface of copper or gold cannot consist of crystal faces.

The upper 20-40 Å. is either pseudo-liquid, or else is composed of minute non-oriented crystals not bigger than 15 Å. This may reasonably be called an amorphous layer by comparison with the metal beneath.

2. The Mechanism of Polishing.—The orientation is presumably due to deformation of the micro-crystals. Since no crystal direction becomes oriented with respect to the direction of polishing, it seems likely that the deformation is pure compression in a direction normal to the surface. Now it is well known ⁷ that slip in a compressed crystal of copper or gold does cause a 110 direction to approach the direction of compression. In order to bring the 110 directions within 20° of the normal to the surface, as in copper, it would not require a great deal of distortion, but a pressure of the order of 10,000 lb. per square inch would be needed. Since the mean pressure exerted when polishing is only about 2 lb. per square inch, the area of metal which is actually in contact with the polishing agent must be about 1/5000 of the total area. Also, there must be very little friction at the points where this large pressure is exerted, or the resultant compressing force would not be normal to the surface.

In the case of gold, the oriented layer is very thick, and it is possible that most of the smoothing of the surface is done simply by the compression. Copper, however, has a much thinner oriented layer, and most of the smoothing is probably done by a very fine abrasive action on the part of the rouge; hence the amorphous layer at the surface. Jenkins ⁸ has found that orientation can be produced by polishing a thin layer of graphite powder. The basal planes become parallel to the surface.

If the above explanation of the orientation is correct, it should be possible to obtain different degrees of orientation by using different polishing pressures. The higher the pressure, the greater should be the deformation of the crystals, and so the more perfect the orientation. There might also be a pressure above which the direction of polishing begins to influence the orientation. It is hoped to investigate these questions shortly.

Summary.

Polished surfaces of copper and gold have been etched electrolytically and photographed by electron diffraction. The Beilby layer has been found to be separated from the non-oriented poly-crystalline interior of the metal, by a layer of oriented crystals; the thicknesses of the two layers have been found.

The orientation appears to be due to deformation of the crystals by compression.

It is shown that the actual surface cannot consist of crystal faces.

I wish to thank Professor E. K. Rideal, F.R.S., for suggesting the research, and for giving his encouragement and many helpful suggestions.

I also wish to thank the Department of Scientific and Industrial Research for a grant which made the research possible.

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⁷ G. I. Taylor and Farren, *P.R.S.*, 1926, **111**, 529; and Flam, *P.R.S.*, 1926, **112**, 289.

⁸ *Phil. Mag.*, 1934, **17**, 457.

GENERAL DISCUSSION.

Professor G. P. Thomson (*London*) said: With reference to Professor Finch's paper, I am sure that all who have worked with electron diffraction will recognise the great advances which he has made with technique as described in the first part of his paper. As regards the extra rings to which he refers, I believe I am right in supposing that there may be two different states of extra rings for the same metal. I suppose that, on Professor Finch's theory, these would be explained by the entry of different kinds of gas into the lattice. On the point of nomenclature I should be inclined to say that the existence of sharp rings proves the existence of some kind of compound, and I should regard the apparent broader bands as due to the intermediate stages between the pure metal and the fully formed compound. There is only one point which I wish to criticise, and that is in connection with whether the Kikuchi lines are due to electrons whose first scattering was elastic or inelastic. Professor Finch has shown that the electrons cannot have lost as much as 2000 volts of energy, but on the theory of ionisation by collision one would expect the loosely bound outer electron to be the most effective, and I should expect that the mean loss of energy would be nearer 20 than 2000 volts, an amount which I do not think Professor Finch would be able to detect.

Professor L. S. Ornstein (*Utrecht*) said: I think that the electron diffraction method as it has been developed by Professor Finch is of utmost importance for the investigation of the structure of films. I might ask if allotropic transitions might be a possible explanation of the extra ring phenomenon. Further it seems to me that the determination of the distribution of the intensities on spots and rings in electronic patterns is of fundamental interest, and I should like to ask whether a method has been already developed in this direction. In the Utrecht Institute some work, which seems rather promising, has been done on the density curves for electrons; on the other hand it is possible to develop a visual method for the intensity measurement—comparison of the light intensities of the spots on a fluorescent screen—a method for visual photometry of Röntgen rays and ultra-violet light on this line is under preparation.

The problem of the Beilby layer is rather complicated; it should be possible to get more knowledge of this layer by optical measurement; if it is in reality an amorphous layer, the optical constants should be different from those of the bare metal. It seems probable that it is a layer of strongly disturbed space lattice. Has it ever been compared with the layer originating in the following way? A piece of glass is cleaned thoroughly, then a brush of copper or iron wires is wetted in any oxidising agent (*e.g.*, potassium bichromate) and the glass is pressed against it while the brush is turned quickly on a lathe, a strongly polished layer of the metal of the brush is then formed on the glass—the layer seems to be of the same type as the Beilby layer.

In the case of evaporated tin in very thin layers no Röntgen diffraction patterns are found; for thicker layers, however, we get Debye-Scherrer diagrams, which, however, occur only when the layer is optically opaque. The transition colour of the thin layers is, however, in accordance with the optical constants of tin; it seems therefore that they are formed of crystals which are too small to give rise to Röntgen

patterns. With gold layers analogous phenomena do not arise; this has perhaps something to do with the fact that tin from a gas is formed in a metastable form which, by transition to the stable form, breaks up into small crystallites. To what extent can analogous effects play a part in the problems of electronic refraction? The fact has been discussed whether the oxygen in thin layers is present in compound or solution form—the difference between both seems in solid state rather a matter of definition.

Professor G. I. Finch (*London*) said: The results of experiments in which metal foils heated *in vacuo* did not yield extra rings but gave extra rings in profusion when heated in gases show that allotropy cannot be the origin of extra rings. Furthermore, we have recently succeeded in obtaining excellent extra ring patterns from silver and gold foils which had been used as anodes during the electrolysis of dilute H_2SO_4 .

We have pointed out in our paper some of the difficulties associated with the interpretation of electron diffraction intensities and shown previously¹ how great is the need for caution in making use of such intensity measurements.

I think the failure of X-rays to give patterns with some evaporated films is possibly sometimes due to the thinness of the material available and, more often to the small crystal size. So far, electron diffraction has invariably given patterns with such films, either by reflection or by transmission and often by both.

Professor E. K. Rideal (*Cambridge*) said: Several aspects of the electron diffraction investigation of surfaces may be of great assistance in elucidating the mechanism of heterogeneous catalysis. It is possible to follow accurately the interdiffusion of one metal superimposed on another, and this can be investigated simultaneously with the catalytic activity of the surface. The structure of the substrate of the Beilby layer has been elucidated by Mr. Lees, and although Professor Finch is a little critical, I think he will find in Mr. Lees' reply satisfactory answers to his criticisms. I would like to congratulate Professor Finch on his observations on gas penetration into metal surfaces. The view that activated diffusion takes place into a metal has now been held by many for several years, but the measurements of such processes by rates of sorption of gas are clearly subject to other interpretations. I incline to the view that gas entering in this manner must be chemically combined in the sense that an electronic switch has taken place, the two phases, metal and gas are too far separated from one another in their critical points to render solid solutions of gas in metal a reasonable explanation. If this interpretation be correct it opens up an interesting investigation on the free energy of the surface compound as influenced by its thickness, crystalline or other state and its miscibility with the unchanged metal. It is clear that definite and sharp dissociation pressures are not to be expected, but the gap between a typical Langmuir adsorption isotherm and a true equilibrium dissociation pressure independent of the extent of the two solid phases is a big one and one which requires filling.

Professor L. S. Ornstein (*Utrecht*) said: Professor Rideal has spoken about the liquid-solid critical point. This possibility seems rather improbable—so far no facts are known proving the existence of such a point. It is, moreover, doubtful whether thermodynamical

¹ *Proc. Physic. Soc.*, 1934, **46**, 148.

methods may be applied to surface layers, as is done in the case of colloidal particles. The orientations of different crystallographical surfaces can give rise to different absorption, as, for example, has been shown by Langmuir in the case of the absorption of caesium on tungsten; similar effects would be expected for other surface layers and this would explain some points as yet not understood in the diffraction patterns.

The indication of the half-width of the diffraction line undoubtedly gives an insufficient measure; great progress in optics has been obtained by considering the form of the spectral lines as a whole.

The potential of a metal cannot be described fully by a periodic function alone. The calculations of Madelung-Zernike-Ornstein mentioned in the work of Ewald (*Handbuch der Physik*) show that the periodical potential in the interior of metals drops to an external constant value exponentially. At a distance of the order of that separating the atoms in the lattice, the field is diminished to half of the value it has at the crystal surface. In discussing the reflection of electrons an exact formula of this type should be used.

Mr. J. R. Tillman (*London*) said: I should like to refer to one or two points in this comprehensive paper. The explanation of the circles occurring in certain single crystal patterns given here overlooks one very important point. Equation (13), which is arrived at either by assuming the circles due to one dimensional diffraction, or by regarding them as secondary envelopes of parabolae (themselves envelopes of Kikuchi lines), does not hold in practice. It has been shown to be invalid for the circles obtained from the (101) face of zinc blende² and from the (010) face of stibnite.³ The radius of the circle observed is less than that given by equation (13), which can be represented more accurately by

$$\sin^2 \theta = \frac{2\lambda}{d} \left(\cos \theta + \frac{\lambda}{2d} \right) \quad \text{where} \quad \tan \theta = \frac{r}{L}$$

and d can be associated with the term $\frac{a\sqrt{\Sigma H^2}}{n}$ in the paper. On the other hand, the radii check up extremely well with those calculated from the equation

$$\sin^2 \theta = \frac{2\lambda}{d} \left(\cos \theta + \frac{\lambda}{2d} \right) - \Phi/V,$$

which is derived, assuming one dimensional diffraction by a row of atoms, the mean potential in such a locality being Φ . The voltage associated with the primary electron is V . This equation yields a value of Φ , constant for any one particular circle, and independent of V . It will be seen at once that the radius of any circle will no longer be accurately proportional to $\sqrt{\lambda}$, providing $\Phi \neq 0$.

I was able to obtain four different circles from the (101) face of zinc blende, namely when the incident beam was directed along the (12 $\bar{1}$), (11 $\bar{1}$), (10 $\bar{1}$) and (010) azimuths, and the values of Φ so calculated differed considerably from azimuth to azimuth. However simple considerations of the positions of the zinc and sulphur atoms lying in these tubes gave a very satisfactory explanation of the observed values, both qualitatively and quantitatively.

² Tillman, *Phil. Mag.*, 1935, **19**, 485.

³ Emslie, *Physic. Rev.*, 1934, **45**, 43.

It should be noted that for a camera length of 20 cms., $\lambda = 0.07 \text{ \AA.}$, a circle of radius 2.5 cms. and a value of Φ of 20 volts, the difference between the observed and calculated (from the more accurate form of equation (13)) radii is more than 0.5 mm. and hence quite easily detectable, especially as the actual measurement of the difference does not depend on an accurate knowledge of the position of the centre of the circle. Table I. gives some data for one of the azimuths (12 $\bar{1}$) mentioned above.

TABLE I

λ in \AA	r (observed) cm.	r (calculated) cm.	Φ in volts.
0.0682	2.00 ₁	2.04 ₂	18.0
0.0685	2.01 ₂	2.04 ₉	16.0
0.0703	2.02 ₄	2.07 ₆	21.0
0.0704	2.02 ₈	2.08 ₀	21.0
0.0732	2.08 ₄	2.12 ₅	16.0
0.0732	2.07 ₃	2.12 ₅	19.5
0.0740	2.07 ₅	2.13 ₃	22.5
0.0808	2.18 ₂	2.22 ₇	16.5
0.0824	2.20 ₂	2.25 ₂	16.5
0.0893	2.27 ₅	2.34 ₀	20.0
0.0970	2.38 ₄	2.44 ₅	15.5

Fig. 1 * shows such a circle.

Although I have a few plates taken from the (111) face of fluorspar, similar to those shown in the present paper, I have measured but one. This, however, appeared to give a value of r less than that to be expected from equation (13).

Emslie's explanation contained one rather weak link. He had to assume that the electron became confined to a row of atoms by some almost artificial mechanism. This, however, is unnecessary. After suffering an inelastic collision, at which the loss of energy need be only a few volts, the electron radiates spherically. The only systems of atoms near the centre of the disturbance capable of giving path differences in the form of arithmetical progressions are rows of atoms stretching away from this centre. No second diffraction condition can come into play and the circle cannot therefore be broken up. It is not without significance, I think, that these circles, of which Fig. 2 * is another zinc blende example, are neither distorted nor very much weakened by proximity to or intersection with Kikuchi lines.

This is but a minor point. The one-dimensional diffraction explanation depends for most of its force on the difference between the observed and calculated radii. This difference seems to me to be well established and accordingly the one-dimensional explanation, fitting the experimental data extremely well, must stand. However, more experimental work must be done, and accurate data obtained, before either explanation can be very much strengthened. The use of a very short camera coupled with a large photographic plate will, I am sure, be well repaid in the study of the diffraction of electrons by single crystals.

The reference to etched single crystals is interesting. When

Professor Thomson⁴ obtained a two-dimensional array of spots from etched single crystals of copper and silver, he suggested that the pattern was due to a transmission phenomenon as described in this paper. Germer,⁵ however, suggested that the array of spots appeared because the crystal was imperfect, and that the pattern was that which was to be expected on rotating a perfect crystal during exposure so as to give a variable angle of incidence. Quite recently I⁶ found that etched single crystals of galena and zinc blende also gave cross-grating patterns, but, in addition, sharp Kikuchi lines appeared. Germer's explanation of the spots would require the crystal to be imperfect to one degree or more; such a degree of imperfection would forbid the appearance of any Kikuchi lines. Even more recently Mr. Cochran, working in Professor Thomson's laboratory, has observed Kikuchi lines from an etched single crystal of copper. This evidence can be said to confirm Professor Thomson's original explanation.

I should also like to draw attention to the work of Jenkins⁷ on graphite, which has many points in common with that described here.

Dr. L. Tronstad (*Trondheim*) said: In connection with the examination of polished metal surfaces, may I call attention to the fact that rouge, when used for polishing, has a tendency to give off oxygen to metals. On iron, for instance, the formation of heavy oxide films was shown optically.⁸ As already emphasised by Le Chatelier, the oxides of the highest heat of formation (*e.g.* aluminium oxide) are the most suitable for avoiding surface oxidation of metals during polishing.

In considering the mechanical side of the process of grinding metals, it might further be essential to distinguish between a "cutting" and a "rolling" grain. A "rolling" grain is, for instance, established on hard laps, such as glass, steel, etc., whereas a "cutting" grain is established on softer pads, such as lead, where the grains are embedded in the surface. There might be a slight difference in the structure and the deformation of the metal surface in the two cases of abrasion.

When discussing the properties and the effect of the "Beilby-layer" it is important to bear in mind the fact that the surfaces of metals are usually covered with an oxide film, formed in presence of traces of oxygen, for instance, from air. This film may modify the external metal properties and if the oxygen penetrates more deeply the diffractive properties of the surface for electrons might also be changed. It seems desirable to emphasise that the lack of "oxide-lines" in the diffraction pattern of metal surfaces is by no means an indication of the absence of oxygen. Oxygen, or other gases may, however, be traced by the distortion of the metal lattice.

The thin normal oxide films on metals (10-30 Å.U. thick), which are of great importance for practical application of metals, because of their tendency to render metals passive, and thus protect them against further attack, cannot be investigated by means of fast electrons, which penetrate too deeply. Slow electrons should be more suitable for this purpose, but the difficulties connected with slow electrons, both from the theoretical as well as the experimental side, are well known. It might, however, be of some use to mention a new method

⁴ *P.R.S.*, 1931, **A**, 133, 1.

⁶ *Phil. Mag.*, 1934, **18**, 656.

⁸ L. Tronstad, *Det Kgl. Norske Videnskabers Selskabs Skrifter*, 1931, **1**, 99.

⁵ *Physic. Rev.*, 1933, **44**, 1012.

⁷ *Ibid.*, **17**, 457.

for slow electrons up to 200 volts, worked out for another purpose in Professor Holtsmark's laboratory at The Technical University of Norway. The electron beam is bent in a homogeneous magnetic field perpendicular to the beam, and a perfectly monochromatic and "parallel" beam is selected by slit arrangements. This beam can be shone on to a surface at any angle of incidence and the intensity of the diffracted electrons can be measured in any direction by means of moveable slit-arrangements and a Faraday-cylinder (placed in the same magnetic field), connected with an amplifier system.

It is hoped tentatively to examine thin films on single crystals by this method.

Professor G. I. Finch (*London*) said: We find that high-speed electrons give quite good patterns with oxide films of the order of thickness mentioned by Professor Tronstad.

Dr. V. E. Cosslett (*Bristol*) said: I should like to ask Professor Finch if he has ever found any extra rings in diffraction patterns obtained from evaporated films. If these rings arise from gas occluded in the lattice, as he suggests, it is easy to understand that they would be shown by films obtained by sputtering in a relatively poor vacuum. But the evaporation of films usually takes place at a much higher vacuum, and we might expect these rings not to appear in such films. Kirchner makes no mention of extra rings appearing in his work on evaporated films. At the same time it is as well to bear in mind that even at a vacuum of 10^{-5} mm. Hg. the rate of collision of residual gas molecules with the surface is comparable with the rate of deposition of metal atoms from the vapour, even with rapid evaporation. So that even in this case large amounts of gas may be captured in the forming lattice.

The question as whether the occluded gas does or does not enter into compound formation with the metal of the film is very interesting and important. With films prepared in hydrogen or nitrogen, compound formation would not in general be expected. But in films prepared or treated in air, oxide formation might take place, especially as there is reason to believe that in this condition the metal is more porous and much more reactive than in the bulk state. In the case of indium I have found evidence of this occurring: a film deposited *in vacuo* was exposed to air at ordinary temperature and pressure for a few hours, after which it gave a well-defined diffraction pattern (Fig. 3*), which proved to correspond to indium oxide, In_2O_3 . The calculated lattice spacing was 10.15 Å., as compared with 10.12 Å. given in the literature.

As indium does not normally oxidise with such rapidity we must regard the metal in thin films as being in a specially reactive state. If this holds true for other metals also, it is possible that some at least of the extra rings found by Professor Finch after heating films in air may be due to oxide formation. Since indium forms the oxide so readily at room temperature, it would not be surprising if gold behaved similarly at 500° C.

I should like to refer also to the production of black rings, mentioned by Professor Finch, who has found them on occasion in transmission patterns. Twice recently I have obtained plates showing a number of such rings, as in Fig. 4† (indium oxide). But it will be

* Plate XXX.

† Plate XXXI.

seen that only the rings of lower order and corresponding high intensity appear black; the outer, less intense rings are normal,—white on a dark background (hardly visible in reproduction). I think that this behaviour may be due to photographic reversal in the emulsion, such as is often observed on over-exposure to a light-source. I should like to ask Professor Finch if his black rings might not be attributable to a like effect, and not to extinction phenomena.

Professor G. I. Finch (*London*) said: The unsteadiness of the cold-cathode discharge referred to by Professor Thomson as occurring above 45 KV. can, we find, be eliminated up to voltages exceeding 80 KV. by maintaining a sufficiently rapid flow of leakage gas through a discharge chamber of suitable design. Thus, at the Physical Society's Exhibition in 1933 we exhibited a cold cathode oscillograph operating continuously for long periods between 70 and 80 KV. without experiencing any unsteadiness in the discharge; also, whilst most of our cameras are operated between 45 and 55 KV., one is usually worked at 65 to 75 KV. because the camera is rather long for the size of plate accommodated.

Metal films prepared by evaporation *in vacuo* have not given extra rings though they do so on subsequent heating in contact with a gas.

We have dealt with the question of the way in which the gas is occluded, partly in our paper and partly in replying to Professor Thomson. Some metals, of course, oxidise without showing signs of forming an interstitial solution with oxygen, but then they yield ordinary oxide patterns and not extra ring patterns.

Photographic reversal cannot afford an explanation of the "extinction" ring phenomenon, because in our Fig. 35 (Plate XIII.) the black ring appears in a position where no intense ring is to be expected and, furthermore, between this extinction ring and the *white* central beam spot there are several strong white rings.

Mr. R. Beeching (*London*) said: I should like to add to what Professor Thomson and Professor Finch have said, with reference to Kikuchi lines. Professor Finch suggests that the lines are caused by double elastic scattering. While I agree with the suggestion, I think that the evidence, upon which it is based, is inconclusive. As Professor Thomson has pointed out, even if the first scattering were inelastic, it is improbable that the resultant broadening of the line would be detectable.

There is, however, one line of argument which seems to lead to the conclusion that both scatterings are elastic. The lines in the pattern, not only interfere with themselves, but they also influence the spots. Thus, when several Kikuchi lines pass through a spot, it becomes star-shaped, on account of the spreading of the intensity along the lines. A much more suggestive effect, is the partial suppression of a spot, by the proximity of several Kikuchi lines. It has been observed, in the case of reflection from the (111) face of diamond, that when an intersection of Kikuchi lines occurs, on either side of the 4th order diffracted spot, the spot loses intensity to a marked extent, while the intersections of the lines become very intense. This effect is shown in the photograph (Fig. 5, Plate XXXI.), which shows the spot when normal and when partially suppressed by the closeness of the intersection of the lines, the exposure time in each case being the same.

This leads to the conclusion that the spots and lines are due to coherent radiation, otherwise such interference could not occur. Since

the spots are due to elastic scattering, the lines must also result, partly at least, from purely elastic scatterings.

It should be pointed out that on the simple theory of diffraction, it is not correct to speak of double elastic scattering, since it is assumed that an electron, once scattered, goes into a Laue direction and is not scattered again. J. W. Harding has suggested that diffuse radiation, resulting from elastic scattering, might be caused by the thermal agitation, and this diffuse radiation might give rise to the Kikuchi lines.

Professor F. Kirchner (*Köln*) (*communicated*):

ELECTRON REFLECTION ON POLYCRYSTALLINE METAL LAYERS AND SURFACE STRUCTURE OF POLISHED METALS.

On exposing a polycrystalline metal layer to a narrow beam of fast cathode rays under a sufficiently small angle one fairly frequently obtains a relatively well-defined powder diagram with sharp interference rings. As is well known, G. P. Thomson⁹ has explained this by assuming that many small lumps project from the surface, the lumps being thin enough (10^{-7} - 10^{-5} cm.) to be passed by the cathode rays without considerable scattering. If the lumps are removed, *e.g.*, by carefully polishing the metal surface, the interference rings become more and more diffuse, as French¹⁰ and Raether¹¹ have shown; finally there remain only two very broad and weak interference maxima which have the same position for nearly all metals investigated. The explanation proposed by French and Raether, and now generally accepted, is that the polished metal surface is in an amorphous or liquid-like state, the mean distance of the atoms of some metals being supposed to be very much smaller than in the molten state of the metal. As recent experiments by Finch, Quarrell and Roebuck¹² and by Hopkins¹³ and Lees¹⁴ apparently supported this explanation, the electron diffraction experiments were considered to have furnished an experimental proof for the existence of an amorphous surface layer on polished metals, as was expressed in this discussion.

My own experiments, however, are not in agreement with this conclusion. Some years ago¹⁵ I called attention to the fact that with respect to the broadening of the interference lines there exists a marked difference between reflection and transmission. Neglecting the broadening caused by deformation of the crystal lattice, one can, from the broadening in the case of transmission, draw a definite conclusion as to the size of crystal grains. In the case of reflection, however, a broadening might just as well arise, *e.g.*, at large crystal grains, from the projecting of only a small part of the grain or from refraction at the surface of the grain. Therefore, no definite conclusions can be drawn as to the size of crystal grains within the surface layer so far as reflection experiments are used.

The simplest conditions of interference are found on the surface of fresh metal layers produced by condensation in a high vacuum, as

⁹ G. P. Thomson, *Proc. Roy. Soc.*, 1930, **128A**, 641.

¹⁰ French, *ibid.*, 1933, **140A**, 637.

¹¹ Raether, *Z. Physik*, 1933, **80**, 82.

¹² Finch, Quarrell and Roebuck, *Proc. Roy. Soc.*, 1934, **145A**, 676.

¹³ Hopkins, this vol., p. 1095.

¹⁴ Lees, *ibid.*, p. 1102.

¹⁵ Kirchner, *Nature*, 1932, **129**, 545.

their naturally grown structure is not yet altered or destroyed by mechanical treatment or other influences. Some years ago I described the following experiment.¹⁶ Polycrystalline gold films of about $1 \cdot 10^{-6}$ cm. thickness were subjected, under like conditions, to rapid electron streams, on the one hand by transmission, and on the other hand by reflection. The transmitted rays furnished sharp interference rings (111 and 200 were clearly separated), whereas the reflected rays gave only two very diffuse and broad maxima¹⁷ of the same nature as those which can be obtained from well-polished layers. Since no structural difference can exist in a layer of a thickness of only 100 Å.U., this experiment indicates that the *same* structure gives, with reflected rays, diffuse rings and with transmitted rays sharp interference rings.

As, however, the possibility that the diffuse maxima obtained by reflection may have been due to a thin layer of organic matter condensed on the surface seemed not to be wholly excluded, I induced Mr. W. Papsdorf to repeat the experiment. The fairly extended experiments which will be mentioned in detail by Mr. Papsdorf in his thesis, definitely confirmed the former results: very thin metal films, condensed under like conditions on the same support, furnished broader interference rings in reflection than in transmission. The difference diminishes as the thickness of the film increases; at any rate, "sharp" interference rings appear under the same conditions at a larger thickness in reflection than in transmission. (I made the same statement in an earlier systematic research on the structure of various metal films condensed in a high vacuum.)

An explanation can easily be given. Assuming an ideal smooth support, *e.g.*, a mica cleavage plane, the original roughness is of atomic order. If, at the beginning, the crystal grains are comparatively small, the roughness of the surface will correspond to about the size of the crystal grains (one may compare the surface of a vessel filled with corn); consequently at grazing incidence nearly all grains will be covered to such an extent by their neighbouring grains, that they can contribute to the interference effect only with their utmost peaks and not with their whole size. Supposing for instance that only one quarter of the grain diameter is hit by the electron beam, we can easily see that in reflection a certain sharpness of the interference lines can result only at considerably greater dimensions of the grains than in transmission. Therefore one cannot draw any definite conclusion from reflection experiments as to the size of the crystal grains even in the case of a naturally grown metal surface; and the broadening actually observed on mechanically treated and polished metal surfaces can by no means be considered as an experimental proof for the existence of a surface layer with extremely small grain-size, or of an amorphous or liquid-like layer.

Other investigations by W. Papsdorf and myself seem to indicate that such an amorphous layer cannot exist on polished metals, since we have found that layers giving strongly broadened interference rings in transmission, *e.g.*, red coloured transparent films of amorphous selenium, furnish in reflection no interference maxima at all, but only a continuous diminution of intensity. Mercury surfaces, too, gave no interference maxima but only a monotonous decrease of intensity toward larger scattering angles, if they had been carefully cleaned by

¹⁶ *Erg. exakt. Naturwiss.*, 1932, 112.

¹⁷ *Loc. cit.*, Fig. 40.

allowing the mercury to flow over in a high vacuum. If a smooth amorphous or liquid layer existed on the surface of polished metals, we should therefore expect no interference maxima at all; the maxima actually observed can therefore be considered as an argument for a remarkably greater degree of roughness of the polished metal surface compared to the surface of an amorphous material or a monoatomic liquid.

Dr. W. H. J. Vernon (*Teddington*) said: The application of electron diffraction technique to the examination of thin films of reaction product has obvious possibilities for the elucidation of problems in atmospheric corrosion. The paper by Professor Finch and his collaborators shews the great progress that has been made in matters of technique since the observations of Professor G. P. Thomson in 1928. I should like, however, to support Professor Desch in urging that still more attention be given to the study of surface oxide films, the existence of which has been demonstrated by other methods. It is to the electron camera technique that one looks for information concerning the nature and structure of such films that is not available in any other way. In a previous paper¹⁸ Finch and Quarrell showed that the first product of oxidation of a zinc surface in air (within the first few hours) is an oxide film that is basally pseudomorphic with the underlying metal. Probably they were scarcely justified in speaking of the "well-known corrosion-resisting properties of zinc" for the behaviour of this metal is usually judged by contrast with iron which it is so largely employed to protect. Under atmospheric conditions, comparable with those for which Finch and Quarrell investigated the primary oxide film, it has been found¹⁹ that zinc gives a linear relationship with time from the first day onwards, whilst the resulting secondary film has a granular structure. The gravimetric method was not sufficiently sensitive to follow the changes during the first day, but as the straight line gives an intercept on the vertical (corrosion) axis, it is evident that something "different" happens in the very early stages; particular interest therefore attaches to the electron diffraction evidence. The constancy of the linear relationship for any one specimen, and the comparatively small extent by which the rate was affected by seasonal changes, were always matters for some surprise; clearly these cannot be accounted for by any property of the (secondary) granular film. If, however, it is postulated that the rate is controlled by the underlying pseudomorphic oxide in immediate contact with the metal, then the evidence as a whole becomes explicable. A similar explanation has already been advanced by Tronstad and Höverstad;²⁰ I should like, however, to emphasise the close agreement that appears to exist between the gravimetric and (so far as it has gone) the electron diffraction evidence, and to express the hope that still more work of this nature may be forthcoming.

Professor G. I. Finch (*London*) said: The linear rate of corrosion of zinc seems to be in fact a measure of the rate of conversion of the self-healing, densely packed, pseudomorphic zinc oxide film to the loose and porous, indeed, granular form of zinc oxide.

Professor Thomson, in reply, said: It seems to me possible that the diffuse maxima obtained by reflection by Professor Kirchner may

¹⁸ *Proc. Physical Soc.*, 1934, **46**, 148.

¹⁹ *Trans. Faraday Soc.*, 1927, **23**, 135.

²⁰ *Ibid.*, 1934, **30**, 1122.

have been due to a thin layer of organic matter condensed on the surface; if very thin it would probably not give any appreciable effect by transmission.

I have difficulty in accepting Dr. Kirchner's new explanation, at least in so far as it refers to the broad rings formed on polished metals. Since there is no appreciable effect of refraction, the surfaces through which the electrons actually pass must make angles exceeding about 5° with the electron beam. Taking the effective penetration of the electrons at 4×10^{-6} cms. and the angle as 5° the depth of the part of the crystal affected would be at least 2×10^{-7} cms. and this would be sufficient to give very much sharper rings than are, in fact, observed on a polished surface. Furthermore it is very difficult to say how a surface can, in fact, be built up of blocks inclined at angles of about 5° - 10° without using some kind of amorphous structure as cement, and this would presumably, be contrary to Kirchner's views. It is also rather difficult to see how such a structure could give rise to rings of sensibly uniform intensity round the circumference, as one would expect that the planes which lie near the surface would belong to a few simple crystalline types.

Professor Finch, in reply, said. When a metal such as gold is heated in contact with a gas different sets of rings are obtained, according to the nature of the gas. The sharpness of the rings by itself hardly suffices to prove the existence of a compound; alloys can also give sharp Debye-Scherrer patterns. Recently we have obtained extra rings from gold heated in argon. This, together with the fact that extra rings due to oxygen in aluminium are easily removed by heating to only 500° C. in hydrogen, and that the extra ring pattern is usually preceded by a band pattern, *i.e.*, evidence of expanding lattice dimensions, seems to me to be conclusive evidence in favour of the interstitial solution view and against the idea of compound formation.

The "one-dimensional" ring should be about 1 per cent. smaller in diameter than the ring formed as secondary envelope by the Kikuchi lines. Therefore, according to the "one-dimensional" view, two rings with corresponding separations should appear in the fluorite patterns in our paper. Only one ring appears, however; yet the definition of these patterns (for example, Fig. 7*) is such that rings of this order of separation would be easily resolved.

By direct experiment we were only able to find that the first scattering was elastic to within 200 in 60,000 volts. I am very glad to see Mr. Beeching bringing forward what seems to me to be convincing evidence of the elasticity of the first scattering.

The simple theory of electron scattering is, as W. L. Bragg has pointed out (*The Crystalline State*, p. 263) altogether inadequate.

Mr. J. R. Tillman (London) said: The table of values of ϕ (Table I. given by Professor Laschkarew) obtained by the diffraction of fast electrons is hardly representative of the work that has been done, nor does it shew the good agreement that has been reached for almost every substance examined. Unfortunately the author has included in his table certain values which, based on very little experimental data, are of little weight. Accordingly I must include Table II. showing the more thorough results for rock salt, calcite and zinc blende.

A more complete table has been given quite recently by Professor Thomson.²¹

* Plate II.

²¹ *Nature*, 1935, 135, 492.

TABLE II.

	Yamaguti.	Shinohara. ²²	Tillman. ²³
NaCl . . .	7.7 ± 0.1	6.3	7.2 ± 0.2
Calcite . . .	12.4	13.8	12.9 ± 0.4
ZnS . . .	12.7	12.2 (Kikuchi and Nakagawa)	12.6 ± 0.15

Moreover one infers from the paper that the differences in the values of ϕ for zinc blende obtained by various workers might be explained by wrong ordering of the diffracted spots. For zinc blende, at least, this is absurd. Equation (2) may be written

$$V \sin^2 \theta = n^2 \frac{150}{4a^2} - \Phi.$$

Now for zinc blende $\frac{150}{4a^2} \sim 10$ volts, and in practice one obtains values of $V \sin^2 \theta$ of about 30, 80, 150 and 240 volts—in addition to one very much smaller. One immediately assigns order numbers 2, 3, 4 and 5, giving a value of Φ of about 10 volts. It will be seen at once that any other ordering leads to an impossible value of ϕ . In the same way it can be shewn that wrong ordering cannot occur for rock salt, galena, calcite, fluorspar and graphite.

The Kikuchi line method first used by Shinohara deserves attention. It is free from many of the difficulties associated with the better known method, which depends on observations on the diffracted spots. Moreover it has been shown²⁴ to give almost identical values of ϕ as the spot method for the same specimen.

The method of calculating the mean grating potential given here, resembles very closely that used by Shinohara.²⁵ Indeed I am very surprised to find no mention of Shinohara in the whole paper. He obtained a quite rapidly converging series, using the X-ray atomic scattering factors, and his calculation for rock salt, which took into account the vibrations of the nuclei, gave a fairly satisfactory value of Φ . It must be noted, however, that the models of the ions adopted are not of extreme importance, providing they do shew in a rough way the correct falling off of electron density with increasing distance from the nuclei. Quite recently I²⁶ have had cause to use a very simple model of an ion, which assumed that the electron density at a distance r from the nucleus was proportional to $(a - r)/r^2$ where a was the ionic radius. This model gave a value of Φ for zinc blende of 9.6 volts and for rock salt of 7.7 volts! Thus the ability of any model to give a reasonable value of Φ for such a substance as rock salt cannot be taken as a measure of its accuracy.

Dr. V. E. Cosslett (*Bristol*) (*partly communicated*):

²² *Sc. Pap. I.P.C.R.*, 1932, **18**, 315.

²⁴ Tillman, *loc. cit.*,²³

²⁶ Tillman, *Phil. Mag.*, 1935, **19**, 485.

²³ *Phil. Mag.*, 1934, **18**, 656.

²⁵ Shinohara, *loc. cit.*

A NEW DIFFRACTION EFFECT WITH SODIUM CHLORIDE.

It was shown by Kirchner²⁷ that an electron diffraction pattern could be obtained from sodium chloride by allowing a dilute solution to evaporate on a very thin celluloid film held in a metal holder, and then passing an electron beam through the layer of salt crystals that is formed. Concentric rings are obtained on the observation screen, as in an ordinary powder photograph.

In attempting to use such a salt film as a standard for wave-length calibration in electron diffraction experiments, I observed unusual variations in the lattice spacing calculated from the diffraction rings recorded on a photographic plate. This spacing proved to be much smaller for the rings of lower order than for the outer rings, as shown in Fig. 6; the difference between the innermost and outermost rings measured was approximately 2.5 per cent. Such a disagreement amongst results from measurements on the same plate could

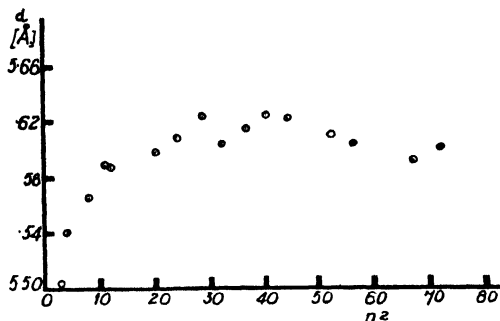


FIG. 6.

not arise from any error in voltage reading or camera length; nor from shrinkage of the photographic emulsion or from secondary effects in the supporting layer of celluloid, as no such irregularities were found for continuous films of metal or metal oxide deposited and photographed in the same way.

The appearance of the diffraction rings obtained (Fig. 7 *) suggested a possible cause of the effect. It will be seen that they are not continuous, but are composed of many separate spots or flecks. It seemed, therefore, that the pattern might be due not to transmission but to reflection of electrons by the salt crystals. The large amount of diffuse scattering about the direct beam also pointed to reflection taking place, being much more intense than true transmission photographs show. It is well known that reflection of electrons from a crystal surface normally gives a pattern of spots, unless the crystal is perfect to a high degree, when a pattern of lines appears as well. These spots lie on circles concentric about the spot made by the direct beam. It is clear that if the diffracting crystal were slowly rotated about an axis lying in the incident beam of electrons, the diffraction spots would progress around the circumference of the circles on which they lie; in the limit continuous circles would be recorded on the plate. The same effect would be produced if the electron beam were simultaneously reflected from a large number of separate crystals all having a face inclined at approximately the same small angle to the incident beam, but otherwise in random orientation about the axis of the beam.

²⁷ Kirchner, *Naturwiss.*, 1930, 18, 707.

* Plate XXXII.

It is probable that crystals growing out of a dilute salt solution would fulfil these conditions. A large number of separate crystallites would form, resting on identical faces (especially probable in the case of a cubic structure such as that of salt), and with sufficient space between them for electrons to pass and suffer reflection from the crystal faces standing roughly perpendicular to the supporting film. The diameter of the electron beam in the plane of the specimen is about 1.5 mm., in which area the requisite large number of crystallites could easily be found. Such reflection of electrons passing through the spaces between separate crystals would be in many ways similar to reflection in the pores of a perforated film, as discussed theoretically by G. P. Thomson.²⁸

If the observed pattern is indeed formed by simultaneous reflection from many crystallites orientated in this way, two possible explanations of the variation in spacing present themselves, which will be considered separately.

(a) In the process of reflection the electrons will also suffer refraction in the crystal surface. The amount of this refraction will be governed by the inner potential of the lattice ϕ . The usual Bragg relation

$$2d \cdot \sin \theta = n\lambda \quad (1)$$

becomes modified in the case of simple refraction, now being

$$\sqrt{\sin^2 \theta + \frac{\phi}{V}} = \frac{n\lambda}{2d} \quad (2)$$

where θ = angle of reflection, d = lattice constant, n = order of reflection, λ = wave-length in Å., and V = corresponding voltage, as calculated with the use of the relativity correction.

If now the value of ϕ decreases near the surface of the crystal, as suggested by the experiments of Yamaguti²⁹ and of Kikuchi and Nakagawa,³⁰ and by the theoretical considerations of Laschkarew,^{31, 32} then the apparent crystal spacing would increase rapidly with increasing order of reflection

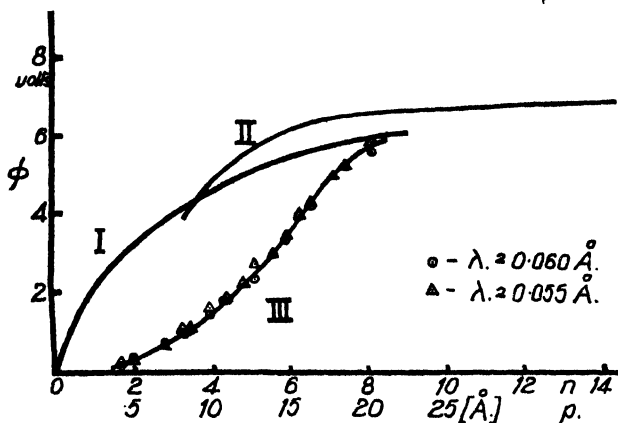


FIG. 8.

towards a constant value at high orders. The elementary treatment of Laschkarew³² of the variation of ϕ in the periodic field of a one-

²⁸ G. P. Thomson, *Phil. Mag.*, 1928, **6**, 939.

²⁹ Yamaguti, *Proc. Phys. Math. Soc. Jap.*, 1932, **14**, 1; 1934, **16**, 95; 1935, **17**, 58.

³⁰ Kikuchi and Nakagawa, *Z. Physik*, 1934, **88**, 757.

³¹ Laschkarew, *Z. Physik*, 1933, **86**, 797; 1934, **89**, 820.

³² Laschkarew, this volume, page 1081.

dimensional crystal gives curve I (Fig. 8) for the variation of ϕ with order. The experimental curve of Kikuchi and Nakagawa³⁰ for molybdenite has the form of curve II (on a comparable scale). The values of the inner potential for the different orders in the diffraction pattern of salt were calculated from equation (2) for two plates obtained at different voltages. The resulting curve III is shown in Fig. 8.

It will be seen that the form of the upper part of the experimental curve III begins to approximate to that of Kikuchi's curve II. How near this curving over towards a "saturation" value would bring curve III to the most recent values given for the mean inner potential of rock salt (7.2 to 7.7 volts) cannot be estimated with any accuracy. But there is no great difference in the upper part of the three curves. On the other hand, the decrease in ϕ at low orders is much greater than any theoretical considerations can justify. It is possible to make a rough calculation of the depth of penetration p of the electron beam in a direction perpendicular to the surface of the crystal for the different orders, *i.e.*, for varying angles of incidence θ . If the depth of penetration in the direction of the electron beam is t , then

$$\sin \theta = \frac{p}{t}.$$

The values of $\sin \theta$ are known from experiment, and as a rough approximation for t we can take 500 Å., from the estimate given by G. P. Thomson³³ for the maximum distance an electron can travel in a lattice before suffering an inelastic collision. Such a calculation yields a value for p of 5 Å. for the second ring (002; $n = 2$). On the basis of this, the depth of penetration of the beam perpendicular to the crystal surface is rather tentatively given as abscissa, corresponding to the order of reflection n , in Fig. 8. From the curve III it would follow that the value of ϕ was only 0.3 volt. at a distance of 5 Å. from the crystal surface, *i.e.*, in the second layer of atoms. This is clearly much less than can be possible in fact. The most recent value³⁴ for the mean inner potential of rock salt is 7.2 volts.

Hence the refraction effect, even though it may play a part in affecting the position of rings of higher order, is not large enough to account for the shift of the lower orders.

(b) It is possible that the effect shown in Fig. 6 is a true spacing effect. That is, the lattice constant may actually assume smaller values towards the surface of the crystal. Lennard-Jones and Dent³⁵ have calculated the contraction in the lattice of rock salt that would occur in the surface layer of atoms, and between this layer and the next within the surface. They find a contraction of about 5 per cent. in each case. Now it has been shown above that at very small angles of incidence, or low orders of reflection, the electron beam can only penetrate to a depth of two or three atomic layers perpendicular to the surface. In this surface lattice it seems probable that the effective lattice spacing would be 2-3 per cent. less than normal, since at the actual surface we expect it to be 5 per cent. less. As the experimental variation in spacing is about 2.5 per cent., it is clear that this surface contraction could account for the anomalous values found for low orders. Beyond the first few orders, however, this contraction will rapidly diminish, and some other

³³ G. P. Thomson, *Phil. Mag.*, 1934, **18**, 640.

³⁴ Tillman, *Phil. Mag.*, 1934, **18**, 656.

³⁵ Lennard-Jones and Dent, *Proc. Roy. Soc.*, 1928, **121**, 247.

explanation, such as the refraction effect, is necessary for the variation in spacing with higher orders.

It seems justifiable to conclude that both the refraction effect and the contraction of the lattice at the crystal surface contribute toward the experimentally observed variation in lattice spacing. Unfortunately the present accuracy of voltage measurement (1 per cent.) is not such as to make possible a determination of the extent to which each factor is effective. But it is plain that this diffraction effect offers interesting possibilities of exploring the way in which the inner potential of a lattice on the one hand, and the lattice spacing on the other hand, decreases from the interior of a crystal towards its surface.

Professor W. E. Laschkarew (*Leningrad*) (*in reply, communicated*): Mr. Tillman says that Shinohara's³⁶ method of calculating the mean potential from X-ray data, which was not mentioned in our work, gives a quite rapidly converging series from which reasonable results for NaCl may be deduced. However, if we take the measured values, reduced to absolute zero, including also zero point energy³⁷ for atom factors of NaCl, then we obtain the following numerical values for first six terms according to Shinohara's series:

$$22.7; -31.3; 25.0; -19.9; 16.7; -13.8 \text{ volts,}$$

the sum of which is equal to -0.6 volts instead of 7 volts, obtained experimentally. Thus, nearly the whole value of the mean potential must be obtained by extrapolation of the atom factors for the higher orders. Such extrapolation demands high accuracy because of the peripheral electrons, the distribution of which determines the greater part of the mean potential, and has an exceedingly small influence on the values of the atom factors for the higher orders. This makes the results obtained very unreliable. We are sure that our method of the "equivalent" atom, which differs in principle from that of Shinohara, is free from this defect.

We are very much surprised that the simple model of an ion used by Mr. Tillman³⁸ gave for the mean potential of ZnS and NaCl values which are in such good agreement with experiment. It is not quite clear why the values of the mean potential, obtained by the electron diffraction method by various authors are different for the same substance. I am in agreement with Mr. Tillman that this could not be explained by wrong ordering. In this connection the recent work of Yamaguti³⁹ in which he found values for ϕ for different specimens of pyrites from 2.7 to 11.2 volts is especially interesting. These values are reproducible with each specimen. Yamaguti explains this fact by the occurrence of impurities in the surface layer of the specimen.

Professor G. P. Thomson (*London*) said: As regards the papers by Mr. Lees and Mr. Hopkins, it is gratifying that they agree so well in the measure of the thickness of the Beilby layer, and I hope that the existence of this layer can now be regarded as an established fact.

Professor R. W. Ditchburn (*Dublin*) said: The destruction of the Beilby layer by sputtering may consist partly in removal of material and partly by local heating causing crystallisation. The latter effect does not appear to have been considered by Mr. Hopkins. According

³⁶ K. Shinohara, *Sc. Pap. I.P.C.R.*, 1932, 18, 315.

³⁷ I. Waller and R. W. James, *Proc. Roy. Soc.*, 1927, 117, 214.

³⁸ I. R. Tillman, *Phil. Mag.*, 1935, 19, 485.

³⁹ T. Yamaguti, *Proc. Phys. Math. S.J.*, 1935, 17, 58.

to Von Hippel's theory,⁴⁰ sputtering really consists in local boiling, and even if we do not accept this theory in detail, it is certain that a positive ion of 2000 volts is stopped and its kinetic energy converted into heat very close to the surface. The extent to which this heating will produce melting followed by recrystallisation depends on the rapidity with which heat could be conducted away. A rough calculation indicates that the local heating effect may account for most of the results obtained by Mr. Hopkins. If Mr. Hopkins believes that the destruction of the Beilby layer is nearly entirely due to removal of material (and not to the effect I have suggested) he could greatly strengthen his position by varying conditions of sputtering (voltage, current, nature of gas) and seeing whether the rate of destruction of the Beilby layer (as measured by diffraction photographs) is always proportional to the rate of removal of material from the cathode. In the meantime it might be as well to regard his result as giving a lower limit to the thickness of the Beilby layer. It should perhaps be stated that electrons with their larger penetrating power would not produce a strong local heating effect.

Dr. A. G. Quarrell (*London*) said: I am worried about the estimates Mr. Lees gives in his paper for the sizes of his crystals. I fail to see how Mr. Lees can estimate the size of orientated crystals in view of the abnormal ring-broadening effects produced by inner potential and tolerance in the angle of scattering, in addition to the rings being incomplete and of non-uniform circumferential width. As maximum resolving power is obtained with a length of grating, normal to the beam, of 80 to 100 Å, it is impossible to say that the size of the crystals is greater than 300 Å, on electron diffraction evidence. I feel that it should be emphasised that the method of estimating crystal size from the width of electron diffraction rings is only a very approximate one and that the accuracy implied by estimates of 70, 90 and 100 Å, cannot be attained.

Surely a 5 per cent. solution of KCN has quite an appreciable effect upon gold. After all, the fact that the gold surface appeared unchanged after two minutes immersion means little. We use solutions containing less than 1 per cent. of KCN for thinning gold leaf for transmission purposes; in fact a 5 per cent. solution etches far too rapidly to be of real use for this purpose.

It would have been useful if Mr. Lees had given us a little information about his electron diffraction camera. I should very much like to know if any precautions were taken to free the electron beam from unwanted components such as molecular rays.

Professor G. I. Finch (*London*) said: It might be added to Mr. Lees' summary of previous work that, after carrying out our experiments on the Beilby layer, we concluded that the polished surface is amorphous because our results showed that it has a peculiar property not possessed by a crystalline surface, namely that of being able to dissolve crystals of a foreign metal.

I am afraid that, from the electron diffraction aspect, exception must be taken to Mr. Lees' method of removing the polished surface from gold and copper. We find that in the case of gold, oxygen is driven into the metal giving rise to extra rings, and in the case of copper, anodic oxidation covers the metal with an exceedingly thin film of a copper oxide of uncertain composition. The two diffraction patterns,

⁴⁰ Von Hippel, *Ann. Physik*, 1926, **80**, 672; 1926, **81**, 1043.

Fig. 2 (Plate I.) and Fig. 1 (Plate XXV.) called "Copper-oriented layer" and "Copper" respectively are not really copper but due to this oxide, and in both cases the orientation is similar although more pronounced in the first case. The diffraction pattern of this oxide, shown in Fig. 74 (Plate XVI.), corresponds approximately to cuprous oxide, but the fit is too poor to be certain. It so happens that when this oxide is formed, either by heating or by anodic oxidation of polished or random crystalline copper, it usually appears to take up this orientation. Although the orientation of the oxide crystals may sometimes be influenced by that of the matrix crystals it often happens that no such relationship exists. For example, a single crystal of aluminium in 100 orientation (our Fig. 47) on partial oxidation forms polycrystalline Al_2O_3 , whilst the pseudomorphic form of zinc oxide in effect continues the zinc lattice out of which it is formed, but breaks up into a polycrystalline layer on transformation to the normal oxide. I am afraid that for these reasons we cannot rely upon the deductions drawn by Mr. Lees either as regards the thickness of the Beilby layer or as to the validity of the view which he puts forward on the mechanism of polishing.

There is a further point to which I would draw attention. Mr. Lees gives in Table I. a column of the approximate size of the crystals, and in several cases he arrives at estimates exceeding 100 Å. Now, it is easy to show that in the case of copper, maximum ring sharpness is obtained with less than 100 Å. length of side of the crystal, and even with 80 Å. the ring sharpness should be so great as to differ imperceptibly from that given by a crystal of infinite extent. Furthermore, as far as I can see, apart from correcting for beam cross-section and inhomogeneity, Mr. Lees seems to have overlooked other ring-broadening effects such as variable effective camera length in reflection, refraction and excessive tolerance in the angle of incidence, because, of course, Mr. Lees' patterns are two-dimensional effects. The abnormal width of some of the rings in, for example, our Fig. 70, are to be attributed mainly to the effect of refractive index.

Dr. N. K. Adam (*London*) said: It is worth remembering that Beilby investigated the thickness of the layers on the surface of calcite which were disturbed by polishing, finding that the disturbance extended to 5000 or 10,000 Å. in depth. Most of this disturbed region was not, however, amorphous, but consisted partly of broken and distorted crystal fragments. Judged by his microscopic method, the amorphous layer appeared to be of the order 50 Å. thick.

Mr. C. S. Lees (*Cambridge*), in reply, said: Professor Finch's criticism of my work on gold seems rather irrelevant since my photographs showed no "extra rings," but simply the face-centred cubic series due to metallic gold.

On a number of occasions I have found that electrolysis of gold in potassium cyanide leaves on the gold a film of some compound which I cannot identify. This film can sometimes be removed chemically; an electron diffraction photograph then shows gold rings, again with no "extra rings."

With regard to copper, I can assure Professor Finch that, whatever his Fig. 74 may represent, my interpretation of my own photographs is correct. The captions under two Figs. in question were meant to indicate that these photographs were obtained in my work on copper, and not as interpretations of the photographs. They are perhaps misleading,

but I stated in my paper that "after etching, the rings were always those of cuprous oxide, not copper." The structure of cuprous oxide has been determined by Niggli.⁴¹ The copper atoms lie on a face-centred cubic lattice, and the oxygen atoms on a body-centred cubic lattice; both lattices have constant 4.26 Å. The copper atoms therefore give the usual face-centred cubic series of rings, with their intensities in some cases slightly altered by the presence of the oxygen, which scatters the electrons much less efficiently than the copper; those rings which belong to the body-centred but not the face-centred series will appear faintly.

In Table III. are compared the theoretical radii for cuprous oxide, with the measured radii of a typical photograph of electrolytically etched polished copper.

TABLE III

Theoretical Radius	Measured Radius.	Planes
1.014 cms.	1.01	110
1.24	1.25	111
1.434	1.44	200
1.76	1.74	211
2.03	2.04	220
2.38	2.40	311
2.87	2.86	400
3.12	3.16	331
3.21		420

All my photographs of etched copper have corresponded equally closely to the cuprous oxide structure, and I have never found any evidence of a "copper oxide of uncertain composition."

Professor Finch appears to think that the orientation of my cuprous oxide occurs during oxidation. He says that his "copper oxide of uncertain composition" generally appears to be oriented even though it is formed on unoriented copper. Cuprous oxide however behaves differently, as has been shown by Mehl, McCandless and Rhines.⁴² They find that oxidation of a single crystal of copper (to cuprous oxide) occurs without change of orientation. A layer of oxide as thick as 5×10^{-3} cms. must be formed before it breaks up into non-oriented crystals. As I deal with crystals no greater than 2×10^{-6} cms. the orientation of the cuprous oxide will reproduce that of the copper. Therefore when I obtained oriented cuprous oxide photographs, the copper must have been similarly oriented before oxidation; this orientation must have occurred during polishing.

Professor Finch's last criticism concerns my estimates of crystal size. He states that maximum ring sharpness is given by crystals of 100 Å. This, however, is not a fundamental limit, but depends entirely on the detail design of the apparatus. For my apparatus, the limit is about 300 Å. Not all the measured breadth of the rings is due to the size of the crystals. The rest is due to:—

- (a) Size of incident electron beam, and range of incident angles.
- (b) Inhomogeneity of electrons.
- (c) Length of specimen in direction of beam.
- (d) Refraction.

Each of these effects had been estimated before arriving at the figures given in my paper, although I must apologise for having

⁴¹ *Z. Krist.*, 1922, **57**, 253

⁴² *Nature*, 1934, **134**, 1009.

mentioned only (a) and (b). For instance, the gold photograph of Fig. 3* had rings of half-breadth 0.2 mm. ; about 0.1 mm. of this is accounted for by these factors, leaving 0.1 mm. as the contribution of the crystal itself. Using the approximate relation $x = \text{size of crystal} = \frac{\lambda}{\phi}$, where ϕ is the angular half-breadth, we get

$$x = \frac{0.071 \times 40}{0.01} \times 10^{-8} \text{ cms.} = 3 \times 10^{-6} \text{ cms.} (= 300 \text{ \AA}).$$

It may be mentioned that the better the design of the electron diffraction apparatus, the smaller will be the ring-broadening effects (a), (b) and (c). If these had been reduced to zero, rings of half-breadth 0.2 mm. would indicate crystals as small as 150 Å. ; whereas if I have underestimated effects (a), (b) and (c), then 300 Å. is an *under-estimate* of the crystal size.

I think these remarks also answer part of Dr. Quarrell's question. I agree with him that estimates of crystal size can only be very approximate. He will find that in interpreting my crystal size figures I have not attributed much accuracy to them.

Dr. Quarrell gives no figures for the rate of chemical thinning of gold leaf by potassium cyanide. A solution which etches thin gold leaf "too rapidly to be of real use" to Dr. Quarrell does not necessarily remove the gold as fast as my electrolytic etching. In any case I was chiefly interested in finding whether there was an oriented layer beneath the surface of polished gold ; the thickness of the layer was of secondary importance.

Dr. J. A. Darbyshire (*Manchester*) said : Have any of those who have worked on polish layers recently carried out experiments to determine the minimum time of polishing required in order to give a layer capable of being observed by electron diffraction methods ?

Whilst working on this subject myself I was struck by the comparative ease with which polishing could be effectively carried out sufficiently to give the typical diffuse rings when examined by electron methods.

This seems to indicate that it is easy to produce an amorphous layer of about 10 Å. even before the metal has really taken up a high degree of polish from the optical point of view. I think that systematic measurements of the influence of time of polishing and the pressure used on the thickness of the polish layer ought now to be carried out.

Professor G. I. Finch (*London*) said : I think that we ought to be very grateful to Mr. Hopkins for his admirable survey of the history of the Beilby layer.

In connection with the removal of the Beilby layer by sputtering, it may be pointed out that Guntherschulze⁴² and Von Hippel and Blechschmidt⁴³ have shown that under the influence of ionic drift some of the atoms sputtered into the cathode zone return to the cathode, the number of such metal atoms re-deposited on the cathode increasing with the gas pressure. It is now a well-known fact that the sputtered metal atoms on deposition invariably group into crystals. Thus, Mr. Hopkins' method may possibly lead to an under-estimate of the thickness of the Beilby layers examined by him. Nevertheless, of the

⁴² *Z. Physik*, 1926, **36**, 563 and 1926, **38**, 575; *Z. techn. Physik*, 1927, **8**, 169; *Chem. Zentralblatt*, 1927, **2**, 385.

⁴³ *Ann. Physique*, 1926, **81**, 1001.

* Plate XXIX.

methods hitherto used for the progressive quantitative thinning of the Beilby layer, I do think that the one employed by Mr. Hopkins is the most suitable, because with the relatively low gas pressures employed by him the amount of re-condensation on the cathode was probably very small.

Mr. Hopkins (*London*), in reply, said: As Professor Finch observes, owing to the comparatively low gas pressure I do not consider that in my experiments there was any serious recondensation of metal at the cathode. In any case the thickness of the recondensed layer cannot exceed the small value defined by the condition that the rate of spluttering from below the recondensed layer shall equal the rate of redeposition.

While agreeing with Professor Ditchburn that there is a possibility of some recrystallisation at the cathode surface as a result of spluttering, I think it improbable that this effect is of any great importance. Having removed say 40 Å. from the polished surface we find, in general, that the substrate shows (011) orientation. If there has been appreciable recrystallisation it follows that this orientated layer must have been formed by recrystallisation. We therefore, on this basis, should expect to find (011) orientation independently of depth below the original surface. Actually at depths greater than about 500 Å. the crystals are unorientated. This suggests that recrystallisation is not playing an important part in producing the changes in structure observed.

I should like to mention, in connection with the observations of Dr. Adam, that from electron diffraction experiments on calcite surfaces polished as described by Beilby, I have been unable to find any evidence to suggest that an amorphous layer exists in this case. Indeed, electron diffraction results obtained up to the present suggest that the amorphous layer is formed only on metals (including selenium and silicon).

I cannot agree with Professor Kirchner that an amorphous layer would not give a pattern. From a theoretical point of view we should expect a pattern to be formed of the nature actually found by experiment. Further it is of interest to note that carefully cleaned, vacuum distilled mercury yields diffuse interference rings by reflection.

MOLECULAR LAYERS OF FATTY SUBSTANCES ON METALS.

By J. J. TRILLAT (*Professeur à la Faculté des Sciences de Besançon*) and H. MOTZ (*Boursier de l'Académie des Sciences de Vienne*).

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For several years we have utilised the diffraction of electrons in the study of the structure of thin films of long-chain organic substances such as the paraffins and fatty acids,¹ cellulose derivatives,² and rubber.³ In the same way cellulose has been studied by G. P.

¹ J. J. Trillat and Th. von Hirsch, *J. Physique*, 1933, 7, 38-43 and *C.R. Acad. Sci.*, 1932, 215.

² J. J. Trillat, *C.R. Acad. Sci.*, 1934, 198, 1025.

³ J. J. Trillat and H. Motz, *C.R. Acad. Sci.*, 1934, 198, 2147.

Thomson and Reid,⁴ Dauvillier,⁵ F. Kirchner,⁶ Taylor Jones,⁷ and G. Natta.⁸

Speaking generally, the diagrams obtained with organic polymers (cellulose and its derivatives, rubber and its derivatives, polyoxymethylenes, polystyrols, proteins, synthetic resins) do not agree with the X-ray figures^{2, 5, 9}, although, in certain conditions there is complete accord, as we have shown for rubber³ as well as for the paraffins and fatty acids.¹

The disparity is most characteristic in the case of cellulose derivatives. In studying the different types of diagrams obtained by the diffraction of rapid electrons (30 to 50 kv.) and their transformations as a function of time, we have shown that a thin film of freshly prepared trinitrocellulose or triacetylcellulose gave first, by transmission and under normal incidence, halos (Fig. 5*) of the "amorphous" type, like those observed by G. P. Thomson and Reid.⁴ Little by little there appeared very sharp interference rings, then isolated spots, and, finally, regularly distributed spots, attributable to a single crystal. Figs. 1, 2 and 3* represent these phenomena. Similar results have been found by other authors.^{5, 6, 7, 8}

If we turn the preparation relatively to the incident electron ray, we observe bands permeated by brilliant spots, which vary in position according to the incidence of the electrons (Fig. 4).

By utilising diagrams of single crystals taken under normal and oblique incidence, we have attempted to establish a model for trinitrocellulose as well as for triacetylcellulose. It has so far, however, been impossible to realise a structural scheme which is really satisfactory, and is in complete accord with X-ray results, notably in so far as concerns the period of identity with the axes of the fibre, determined with certainty by X-rays.

We have also established the remarkable identity of the electronic diagrams of trinitro-, triacetyl-, tripropionyl-, and tributyl-cellulose, as well as their resemblance to the diagrams of the paraffins.¹ These observations led us to express certain doubts as to the attribution of these diagrams to the cellulose derivatives. In a publication in collaboration with H. Mark we make these reservations.⁹ They are indeed reinforced by a series of very detailed studies made by G. Natta⁸ and by a long correspondence exchanged with him. The work of this author will appear very shortly and we will not anticipate his conclusions.

Moreover, a certain number of anomalies in the electronic diagrams of metals, of certain oxides, of graphite, etc., have not as yet been explained.

By careful study of the diagrams published by many authors, we can in fact often demonstrate the presence of interference rings or isolated spots coincident with those just described.

The object of the present work is to show that all the anomalies described above have a common origin; we shall study particularly the case of metals, that of organic polymerised compounds being treated

⁴ G. P. Thomson and A. Reid, *Proc. Roy. Soc.*, 1928, **117**, 60, and 1928, **119**, 663.

⁵ A. Dauvillier, *C.R. Acad. Sci.*, 1930, 708; and *Nature*, 1930, **125**, 50, and 1930, **126**, 866. * Plate XXXIII.

⁶ F. Kirchner, *Naturwiss.*, 1930, **18**, 706 and 1931, **19**, 463.

⁷ Taylor Jones, *Phil. Mag.*, 1931, **78**, 641; 1933, **16**, 793, 953.

⁸ G. Natta, *Giorn. di Chimica Industriale ed Applicata*, 1934, **16**, 285.

⁹ H. Mark and J. Trillat, *Ergebn. techn. Röntgenkunde*, 1934, **4**, 69.

by G. Natta. The work now to be described is as yet unfinished and we can but give a rapid and necessarily incomplete survey.

Electronic Analysis of Metallic Films.

When examining by transmission, and under normal incidence, numerous metallic layers of a thickness of a few $\mu\mu$, we have observed new electronic interferences, which are foreign to the ordinary diagram of the metals and are often visible on a fluorescent screen. These interferences appear for the different metals under examination (Au, Pt, Ag), whatever their physical treatment (forging, rolling, electrolytic deposition) and their degree of orientation; they are particularly intense in the case of films which have been aged (some months or years), although they are often observable, though more weakly, with freshly prepared metallic films.

These "supplementary" interferences take the form sometimes of isolated spots (Figs. 6, 7, 8*), sometimes of complete concentric circles of diameter corresponding to the position of the preceding spots (Figs. 9, 10*).

These new interferences observed with metallic films *are identical, in regard to position and intensity, with those obtained with cellulose derivatives* as well as with some other organic polymers such as polyoxymethylenes, polystyrols, etc.⁸

This analogy has led us, after much hesitation, to attribute to all these diagrams a common origin. We are confirmed in this hypothesis by the recent results of G. Natta, and also by the fact that other organic substances, such as rubber,³ paraffins and fatty acids,¹ furnish electronic interferences in excellent accord, this time, with X-ray figures. G. Natta has shown the same thing with derivatives of cellulose, so long as special precautions are taken in the preparation of the films.

Fundamental Experiments.

(A) If we examine with electrons a metallic film giving one of these abnormal diagrams (Figs. 6, 7, 8, 9, 10) and pass a sufficiently intense electronic beam for several minutes on the point studied, we observe that the supplementary diagram becomes weaker and finally disappears completely; in our experiments, this happens in about 10 minutes.† The diagram of the metal, on the other hand, subsists with the same intensity; the phenomenon may readily be followed on the fluorescent screen, and may be recorded by photographs taken at different times.

We obtain the same result on examining a film of trinitro- or triacetyl-cellulose, which gives the usual diagrams (Figs. 1, 2, 3). After a few minutes the spots or rings have completely disappeared, and there remain only three "amorphous" halos (Fig. 5); a neighbouring position on the preparation, which has not been subjected to electronic bombardment, still gives, on the other hand, the crystalline diagram, which disappears in its turn on irradiation.

(B) By operating with great caution, a metallic film may be washed with benzine or ether. This operation also leads to the complete disappearance of the supplementary diagram; if in the same way a

* Plate XXXIV.

† The electrons were accelerated in these experiments by a constant potential of 40,000 volts—intensity, 3-4 milliamperes; diameter of the beam, 0.1 millimetre.

cellulosic film is washed there sometimes appears, at different points of the film, a *quite different ring diagram*. G. Natta, in an unpublished work, has shown that by operating with special precautions, one can obtain cellulosic films giving directly this new diagram, which will correspond truly to the X-ray figures of esters of cellulose. We feel, however, that this identity with X-ray diagrams needs confirmation.

These fundamental experiments indicate that there may exist, on the surface of metallic or organic films, a *very thin layer of a substance of low melting-point, readily soluble, and crystallisable* in time, which brings about phenomena of electronic diffraction which are very intense. It is very remarkable that these phenomena arise in an identical manner, whosoever be the experimenter, whatsoever the laboratory and the apparatus used, so that this unknown substance takes on a somewhat "international" character.

The reticular distances calculated for the different rings are given further (see Table I.); the spot diagrams correspond to a rectangular lattice,^{2, 6, 9} with sides 4.80 Å. and 7.30 Å. These values are exactly those which one of us has obtained with thin films of paraffin studied by transmission¹ (Fig. 12, Plate XXXV.).

Artificial Deposit of Fine Layers of Fatty Substances on Metallic Films.

In order to explain these phenomena we have attempted to isolate the bodies which, spread in thin layers on very clean metallic films, can give rise to diagrams like those described above. By utilising, as support, metals of which the structure is perfectly known and not destroyed by the electrons, we may hope to obtain interesting results.

We have chosen gold, which is not susceptible to attack or to alteration by the majority of chemical agents. We prepared gold foils, 30 to 40 $\mu\mu$ thick, from beaten gold foil thinned by means of a solution of KCN. We took pains to work with the utmost cleanliness, with the precautions used in biology: careful washing and sterilisation of the receiving vessels, pincers and supports—very pure water—contact with the fingers avoided by using rubber gloves, etc. We obtained, thus, films of gold which, by electronic examination, showed no supplementary rings (Fig. 11). This was verified by exploring the film at all points, by using the fluorescent screen and by taking numerous photographs.

Deposit of Paraffin.—Once in possession of a gold film of which the cleanness and purity have been confirmed by electronic analysis, there is placed on this film a drop of ether containing a very small quantity of paraffin of M.P. 55°. This drop is taken from a solution of title chosen so that, spread uniformly on the gold film, a single drop produces by evaporation a bimolecular layer of paraffin (mean thickness 70 to 80 Å).

The metallic film is then immediately examined by electron diffraction (40 KV.); at all points diagrams are obtained (Fig. 14) which are analogous to those described above, and on which there appear very clearly several rings which do not belong to gold. *The diameters of these rings are identical with those observed with the different metallic films studied above*, as well as with those observed for cellulosic or polyoxymethylene films (see Table I., and compare Figs. 14, 15 (Plate XXXV.) and 1, 2, 9, 10). ($d = 4.14 - 3.67 - 2.92 \text{ Å.}$)

It is frequently noticed that these new rings are granular, whilst the interference rings of the metal are formed of continuous lines. On increasing the thickness of the paraffinic layer (using for example a drop of a solution ten times more concentrated), the supplementary rings are considerably strengthened, without their positions being changed (Fig. 15).

We then attempted to form on gold thin layers constituted by *organic molecules, elongated along the carbon atom chain, of the aliphatic type*.

The observations we have made so far are the following :—

Octadecane (saturated hydrocarbon, $C_{18}H_{38}$).—No new diagram appeared, even with a concentrated solution. The M.P. of this body being somewhat low (29°), it is probable that the thin layer assumes the liquid state when it is struck by the electrons

Stearic Acid ($CH_3 \cdot (CH_2)_{16} \cdot COOH$) and **Tristearine**.—Diagrams weaker and more diffuse than those of paraffin, for the same thickness of film (Fig. 16). Measurements made on these rings, which are the only ones visible, still give the equidistances $d_1 = 4.10$ and $d_2 = 3.64$ Å., in good agreement with the X-ray measurements for the more intense rings ($d_1 = 4.1$ and $d_2 = 3.7$ Å.). (See Thesis, Trillat.)¹⁰

Ceryl Alcohol, $CH_3 \cdot (CH_2)_{25} \cdot CH_2OH$.—This alcohol is extracted from beeswax or china wax. It gives a more intense diagram, the rings having the same diameters as those above-mentioned.

Beeswax.—This is a complex mixture containing hydrocarbons, acids, alcohols and saturated ethers, all with very long linear chains. We may cite, chiefly, myricine palmitate, myricic alcohol $C_{31}H_{64}O$, ceryl alcohol $C_{27}H_{56}O$, cerotic acid $C_{27}H_{54}O_2$.

In a bimolecular layer it gives rise to good diagrams, with numerous supplementary rings, susceptible to precise measurement (Fig. 17).

The reticular distances calculated with these different substances spread as thin films on gold are given in Table I., which shows by way of comparison, the reticular distances calculated from electronic diagrams of paraffin (unsupported film), and of nitro or acetylcellulose, as well as the X-ray measurements for paraffin.

TABLE I.

<i>Electrons.*</i>										
Beeswax on gold . . .	4.14	3.67	2.92	2.42	2.35	2.17	2.00	1.87	1.74	1.59 Å
Paraffin on gold . . .	4.14	3.67	2.92	—	—	—	—	—	—	—
Fatty acids on gold . .	4.10	3.64	—	—	—	—	—	—	—	—
Paraffin (film on water)	4.14	3.73	2.95	2.48	2.35	2.21	2.03	1.87	1.79	1.60
Acetyl or Nitrocellulose	4.10	3.60	2.90	2.50	2.32	2.20	2.05	1.86	1.76	1.60
<i>X-Rays</i>										
Paraffin	4.20	3.80	3.0	2.50	—	—	—	—	—	—

* Precision of measurement = 2 per cent.

(For the X-rays only the more intense rings are shewn).

As will be seen, the coincidences excellent. The agreement of the intensities is also excellent.

Cebacic Acid (saturated diacid: $COOH \cdot (CH_2)_8 \cdot COOH$. Gives nothing.

Oleic Acid (saturated acid with double bond :



Liquid at ordinary temperature. Gives nothing.

We have also tried forming on the gold film very thin layers of other organic substances, having molecules of a form quite different from the above. Whenever a supplementary diagram appears, it is no longer similar to those above described ; for example, cholesterol gives a somewhat diffuse ring, corresponding to a reticular distance $d = 5.35 \text{ \AA}$.

These results on the *artificial* formation of thin layers and their comparison with the results on films which are formed naturally on metals or organic polymers, prove that the abnormal diagrams described at the beginning of this paper are due without doubt to the formation, the extension, and the more or less rapid "crystallisation" of very thin layers of certain categories of fatty bodies having the common characteristic of *being composed of linear molecules with long chains of carbon atoms*.

We propose to study these phenomena of diffusion and orientation of different aliphatic bodies on various supports (metals, oxides, cellulose derivatives, etc.) ; we think that this provides a new means of attack for investigating molecular surface orientation and adsorption, in relation to other physical properties.

Interpretation of the Results.

We shall give later a detailed interpretation of all these results. Our work not being as yet complete we only give now a general review.

It appears to be established that the abnormal diagrams observed with metals and other substances are due to extremely thin layers of certain fatty bodies, present in all laboratories, and arising either from handling or from the grease used for vacuum sealing (the latter is not very probable according to our experiments) or perhaps from the laboratory air, or yet again from other ill-defined sources.

Systematic experiments carried out by depositing different long-chain carbon substances on gold provide an explanation of these phenomena.

We know that the majority of long-chain fatty bodies are liable to orient themselves very readily on contact with various supports. Devaux and Langmuir first showed this in their well-known experiments on monomolecular layers ; X-ray work has given much supplementary support (Müller, Saville, Shearer, J. J. Trillat). One of us has studied these phenomena in detail^{10, 11, 12} and has shown that they depend on the chemical nature of the molecule and of the support, as well as on the thickness of the layer, the molecular orientation being specially localised in the neighbourhood of the contact surface. Frequently the direction of the molecules is perpendicular to the support (substances crystallising in orthorhombic crystals, *e.g.* the paraffins). In other cases it is oblique (substances crystallising in monoclinic prisms, *e.g.* saturated fatty acids).

We know, also, that electrons, even rapid ones, are very absorbable by matter, and that the majority of electrons are diffracted in the more superficial layers. The conditions for interference may be

¹¹ J. J. Trillat and A. Nowakowski, *Ann. Physique*, 1931.

¹² J. J. Trillat, *J. Physique*, 1929.

defined by the equations of Laue, the third condition (corresponding to thickness) being of importance only if the layer is sufficiently thick, *i.e.*, if the electrons meet a sufficiency of atoms in their direction of propagation (W. L. Bragg and F. Kirchner).¹³

In our experiments the metallic film was perpendicular to the direction of the electrons. In consequence, if the aliphatic molecules are oriented normally to the surface of the metal, they are disposed also parallel to the incident ray of the electrons. In considering a molecule with 30 atoms of carbon, a frequent case for the paraffins, the electron ray will meet; if the layer is bimolecular, 60 atoms of carbon. Calculation indicates that, in this case, the third condition of interference of Laue ($a \cos \theta = h_3 \lambda$) corresponds to a very marked maximum of zero order, and everything happens, to a first approximation, as for a crossed lattice. In reality the carbon atoms are not disposed in a straight line, but in zig-zags, the distance between two paired or unpaired carbons being equal to 2.5 Å., and the calculation has to take this disposition into account.

The orientation is so much the more complete as the chains are the longer. The lateral van der Waals' forces depend in effect on this length; they contribute to the regular disposition of these chains the one to the other, even in a monomolecular layer (especially if it is solid). We know by the experiments of spreading on water that the chains can come almost into contact, and realise thus a compact assemblage; these experiments furnish the "section" of the molecules, of which the value has been confirmed by X-ray examination.

The dimensions of the terminal group may play a rôle in the separation of the chains; it may be admitted that, for sufficiently long chains, this rôle is only secondary.

Our researches on the formation of bimolecular layers of paraffin on a metal show that, in a plane perpendicular to the direction of the carbon chains, the latter are disposed with great regularity, according to a rectangular network with sides 4.80 and 7.30 Å. Now, paraffin crystallised on water in a film 50 to 100 $\mu\mu$ thick, often presents crystals uniquely orthorhombic, of which the dimensions are $a_1 = 4.84$ and $a_2 = 7.30$ Å.¹ We can, therefore, conclude that, with our fatty films on metals, the disposition of the molecules is similar to that of the molecules of paraffin in a single crystal oriented on water (Fig. 12).

If the body is not pure, but is formed from a mixture of like molecules of different lengths, the general orientation will not be modified; we know, in fact, that greases, mixtures of fatty acid, mixtures of triglycerides or of ethers give good X-ray diagrams (J. J. Trillat).¹⁰ From the point of view of electron diffraction, and in the case where the electron ray is parallel to the direction of the molecules, the phenomenon will still be the same, since the principal factors are the regularity of the *lateral* disposition of the chains and the number of atoms of carbon encountered. It is even probable—as we see also with X-rays—that the presence of like molecules of different lengths hinders the formation of crystals oriented at hazard; one of us has previously shown that this phenomenon explains the lubricating properties of greases and technical oils.

We explain thus the fact that paraffin, beeswax, or fatty bodies, when deposited naturally, give more intense diagrams than hydrocarbons, acids or pure aliphatic alcohols, which crystallise more readily

¹³ W. L. Bragg and F. Kirchner, *Nature*, 1931, 127, 738.

In the case of liquid layers, thermal agitation hinders the regularity of lateral assembly of the carbon chains (oleic acid). We must, however, in every case, expect to observe a diffraction phenomenon brought about *under tangential incidence*; this result was established by Murison.¹⁴ These bands are due to the diffraction of the electronic waves by the atoms of carbon regularly disposed along the chains, and corresponding in effect to an equidistance of 2.5 \AA , which is, as we know, the distance which separates the atoms of carbon from one another. The conclusions of this work are in good accord with those drawn from our experiments.

In particular, this will explain the origin of the interference bands we have obtained under oblique incidence with films of trinitro- or triacetyl-cellulose (Fig. 4); we calculated in this case an equidistance of 2.5 \AA , which would accord with there being a layer of organic molecules with an aliphatic chain, disposed perpendicularly to the surface of the cellulosic film.

Saturated Acids, Saturated Alcohols and Diacids.—What we have just said is applicable particularly to paraffinic hydrocarbons or fatty ethers, of which the tails of the molecules are (CH_3). In the case of the saturated fatty acids, we have long known that in thick layers (0.01 mm. and above), their molecules have a tendency to orient themselves *obliquely* to the support^{10, 11}; this is confirmed by the monoclinic structure of this body, and we know also that two polymorphic modifications, α and β , may exist. The section of the elementary cell, *perpendicular to the axis C*, remains practically constant in dimensions and in form, and remains the same as for paraffinic hydrocarbons.

Since in the case of the very thin layers studied here, we find for stearic acid equidistances identical with those of paraffin, it must be admitted that in this form the molecules of the fatty acids are oriented normally, and not obliquely, to the surface of the metal. This would correspond to an orthorhombic form of the stearic acid. Now, such a form has already been disclosed by X-rays; one of us was able also to show the presence of this form in films of stearic acid obtained on water,¹ by utilising electronic analysis (Fig. 13). It is remarkable that the electronic diagram of this orthorhombic form always appears after irradiation of a monoclinic form by the electron ray; the reticular constants are: $a_1 = 4.9 \text{ \AA}$; $a_2 = 7.3 \text{ \AA}$, in good accord with the results of the present work.

This hypothesis is equally in accord with the experiments of Langmuir, relating to the spreading of monomolecular or bimolecular layers on water.

Diacids.—The chemical constitution of the molecule certainly plays an important rôle, if it is of such a nature as to retard orientation. For example, the saturated diacids which have two terminal COOH groups have a tendency to dispose themselves *flat* on the surface of the metal, which explains why, in this case, no abnormal diagrams appear.

Extension of Fatty Bodies on Metallic Surfaces.—Aliphatic compounds having two terminal CH_3 groups have a tendency to spread rapidly on bodies freed from hydroxyls: this is the case with the metals on which we spread paraffinic hydrocarbons or fatty ethers. Now, these are precisely the bodies which give the most intense abnormal diagrams, even in very thin layers.

¹⁴ Murison, *Phil. Mag.*, 7, 1934, 17, 201.

We explain thus the contamination and the invasion in course of time of the metallic surfaces studied, in presence of fatty impurities common in all laboratories; it is well to draw this point to the attention of all who seek to study the structure or the superficial activity of metals and other bodies. These first experiments serve also to explain the anomalies often noted in publications relative, for example, to new structures or to "forbidden" rings. It is conceivable that, in certain cases, these observations were falsified by the presence of superficial impurities.

There is an identical explanation for the cellulosic films which give such intense electronic diagrams. G. Natta, moreover, will provide in this connection interesting details. We should add the following observation: The point or ring diagrams are very intense with films of trisubstituted derivatives (tri-nitro-, tri-acetyl-cellulose, etc.), whilst they are more feeble, or even non-existent, with less substituted derivatives (di-nitro-, di-acetyl-cellulose, etc.). This is fully explained, if we take into account that the trisubstituted derivatives have no free hydroxyl groups, which is not the case for the disubstituted derivatives; we intend in addition to carry out work to establish more precisely the mechanism of the spreading of fatty bodies on organic films.

We see here the importance, which we have always emphasised in our earlier work, of the superficial physical and chemical structure of matter, from the point of view of adsorption; possibly there exists a relation just as important in the case of catalysis.

Conclusion.

The totality of our experiments leads us to the conclusion that there exist almost always on the surface of metals and of certain organic films, very thin (mono or bimolecular) layers of fatty substances, constituted principally of molecules of the paraffinic hydrocarbon type or waxes. The layers are deposited in the course of time, and, when they spread on the surfaces, they crystallise in a perfect manner, giving rise to very intense electronic diffractions.

The study of the formation, structure and propagation of these layers, invisible by all other means, presents a certain interest, and can be carried out by electronic analysis. These studies will be continued in our laboratory.

GENERAL DISCUSSION.

Professor G. I. Finch (*London*) said: Professor Trillat's extremely interesting results come at an opportune moment when our interest has been fully aroused in the study by electron diffraction of the absorption of gases by metals. He shows us how careful one must be in order to avoid the occurrence of spurious phenomena due to the accidental presence of films of certain fats and waxes. Professor Trillat's ring diameters are independent of the substrate, whilst the dimensions of rings due to absorbed gases depend upon the nature of the absorbing metal and the absorbed gas; thus there should be no real difficulty in distinguishing between the two types of rings, especially since the organic impurity is soluble in ether or benzene. Furthermore, the well-defined bands so characteristic of many of our "extra" ring patterns have, of course, no counterpart in grease rings.

Dr. N. K. Adam (*London*) said: The occurrence of patterns due to grease on the surface of nitrocellulose films seems to me abnormal;

there is no appreciable amount of grease in a properly prepared nitro-cellulose solution and there is no difficulty in obtaining monomolecular films of many cellulose derivatives on aqueous solutions, practically free from grease. Can Professor Trillat say whether, by using particular care to avoid handling the films or exposing them to the unpurified laboratory air for more than a few minutes, patterns due to nitro-cellulose can be obtained, free from intruding grease patterns? When grease patterns are present, can they be removed by washing with such solvents as carefully purified benzene?

Dr. L. Tronstad (*Trondheim*) said: By means of the optical reflection method C. G. P. Feachem and myself have studied fatty films on clean mercury. By focussing the microscope of the analyser system of the instrument directly on the surface we found¹ with myristic acid, for instance, patches of different thickness, which roughly corresponded to: 1. A monolayer, in which the molecules should lie flat on the surface. 2. A monolayer of the same order of thickness as the chain-length, in which the molecules, therefore, should stand perpendicular to the surface. 3. A multi-layer, in which the molecules seemed to be squeezed upon the top of one another in barriers. The patches changed in size by time but finally a stable arrangement was established.

The work referred to shews that the optical method may also be very useful for examination of fatty films on metals, and shews further that such films cannot by any means in all cases be considered to be homogeneous.

Professor Trillat said *in reply* to Dr. Adam: Films of trinitro-cellulose or triacetylcellulose can in fact be obtained practically free from grease by using carefully purified solvents, by degreasing nitrated and acetylated cotton and by avoiding contact of the fingers with the support of the film. In these conditions G. Natta and I have obtained diagrams of a different type, corresponding truly to the pure cellulose compound.²

The supplementary grease pattern observed with cellulosic films can be suppressed by washing the films with carefully distilled solvents. Benzene so purified is particularly suitable, the grease pattern then disappears and there remains only the nitrocellulose or acetyl cellulose pattern. Analogous results are obtained with metallic films.

In reply to Dr. Tronstad: The optical method is undoubtedly interesting, but it does not give results as satisfactorily as the electron diffraction method. An optical method has, moreover, already been used (by G. Bouhet³ who measured the ellipticity of the reflected light).

It is equally certain that grease films are not homogeneous; the study with the aid of electrons shows this definitely.

In reply to Professor Finch: I think the phenomenon described by Professor Finch differs from that which I report in my paper; it has always seemed to me absolutely indispensable, before any conclusions are drawn, to be assured of the complete absence of a layer of crystallised grease. The best method of ensuring this consists in exposing the substance to be examined to the electrons for 10 to 15 minutes; if the surface has become covered with a film of grease the latter is then completely destroyed, as I have shown, and the pattern obtained is that of the pure substance.

¹ C. G. P. Feachem and M. Tronstad, *Proc. Roy. Soc.*, 1934, **23A**, 127.

² J. J. Trillat and H. Motz, *C.R.*, 1935, 1299 and 1466.

³ See Thesis, *Masson éditeur*, Paris, 1930, pp. 116-120.

PART II.—THE STRUCTURE OF METALLIC COATINGS.

THE CRYSTALLISATION OF THIN METAL FILMS.

BY PROFESSOR E. N. DA C. ANDRADE.

Received 11th March, 1935.

In thin films of metals on solid surfaces we have matter in a peculiar state, possessing mobility at temperatures far below the melting-point of the massive metal. It is a familiar fact that very thin liquid films simulate gas properties, but whereas such films must contain fewer molecules than suffice to form a monomolecular layer, the comparatively mobile metal films, which simulate gas properties, may be several atoms, or tens of atoms, thick. Estermann¹ showed that cadmium atoms move freely from a deposited streak onto the free surface at -118°C. , the melting-point of cadmium being 321°C. ; while Cockcroft² showed that cadmium deposited by a molecular beam would move over the surface of a plate into a space protected by a wire.

The experiments of these and other workers do not prove that the surface of a continuous film is mobile, but rather show that metal, at temperatures much below melting-point, can move from places where there is a film many atoms thick (both Estermann and Cockcroft say that a film less than three or four atoms thick is not visible) on to the neighbouring bare surface.³ In the work to be briefly described here, we have shown that the actual surface is mobile at temperatures above a certain fairly definite critical value, which depends to some extent on the thickness of the film.

Thin films, then, offer a favourable ground for the study of the early stages of crystallisation of metals, firstly because the material is sparse, so that large aggregates cannot form, and secondly because the mobility can be easily controlled by temperature and kept very low if desired. Dr. J. G. Martindale and I have therefore investigated the crystallisation of thin gold and silver films heated in vacuo at determined temperatures. These films were deposited by cathode sputtering on various supporting surfaces, or substrates, as they may be called. I had hoped on this occasion to be able to say something on the crystallisation of unsupported films as well, but the work which I am undertaking on this subject, in collaboration with Mr. Walsh, is not yet sufficiently advanced. The information on unsupported films which we are seeking is needed to supplement the results obtained by the diffraction of the transmitted electron beam.

The method which we have used for examining the films is the microscopic one, employing visible light with a wide variety of conditions of

¹ *Z. Physik*, 1925, **33**, 320.

² *P.R.S.*, 1928, **119A**, 293.

³ The surface may need to be sensitised. See Cockcroft, *loc. cit.*, p. 309.

illumination. As against the electronic method this has certain obvious disadvantages. The electron beam enables us to detect the presence of crystallites which are only a few tens of atoms across, and to estimate their size roughly, while the microscope cannot detect isolated units unless they are a few thousand atoms across, except by so-called ultra-microscopic methods of extremely limited scope. The electron beam furnishes information about the spacing of the crystal planes, and about their orientation with respect to the beam, which the microscope cannot give. This is generally realised, but it seems to have been overlooked that the microscope has, in its turn, certain advantages. The electron beam tells us nothing of the distribution, or grouping in space, of the units which it detects: it gives us an average effect for an area of the order of 1 sq. mm. Again, once the linear dimensions of the crystallite exceed a few tens of atoms, the electron beam can say nothing about the size, and the broadening of the lines on which it relies for its estimate of very small sizes can be indistinguishably produced by the presence of disturbed spacings in larger crystals. The two methods, utilising respectively waves of visible light and electron waves, are supplementary: if the one is too coarse to record fine effects the other is too fine to record coarse effects.

There is another point to be considered in connection with the methods of electron diffraction, and that is the possible modification which the heat generated by the method of examination may produce in the film. It may ultimately prove that there is no such effect in most cases, but this has not yet, in my opinion, been clearly established. We can return to this point after considering briefly the effect of heat on the films.

The metals which we used were gold and silver, since they are free from chemical effects which complicate the sputtering of many other metals (notably, *e.g.*, antimony, lead, silicon and selenium. owing to reaction with the residual gas.⁴

Previous workers, however, record extremely variable results with these metals, especially as regards the colours of the films. We have traced this to heating effects, which accompany the sputtering unless special precautions are taken. For example, the pink and purple colours often described for gold films were found by us at the edge of films deposited on thin glass discs which were, by chance disposition, more effectively cooled at the centre than the edges. With the special precautions finally taken by us to keep the anode plate cool, the films were always of uniform and reproducible appearance, the gold films bluish green and the silver films purple by transmitted light.

Most of the films studied were about 50 atoms thick. They were heated in vacuo for periods of an hour or longer, and photographed either by transmitted light or with a ring illuminator, which throws light downwards on the film from all directions. The first step of crystallisation was observed at about 250° to 280° C. for silver films, and at about 400° for gold films. To the naked eye, the metal appears unchanged, but under the microscope small particles, about 1μ across, can be seen. In parallel polarised light these particles show, between crossed Nicols, a dark cross on a light ground, as illustrated in Fig. 1.* This behaviour is characteristic, not of a uniaxial crystal, which shows the "ring and

⁴ Bartlett, *Phil. Mag.*, 1928, 5, 848, in particular has shown that the properties of gold and silver films prepared by cathode sputtering are unaffected by the possession of ordinary residual gases.

* Plate XXXVI.

cross " in convergent light, but of the spherulitic form, exhibited by many natural minerals and artificial precipitates, *e.g.*, copper phosphate particles (Fig. 2 *). A similar appearance is shown by particles forming in a cooling nematic substance, *e.g.*, para-azoxyanisole (see *e.g.*, Sir William Bragg, *Proc. Royal Institution*, 1933, **28**, 57, Plate IV.). A spherulite is an aggregate of uniaxial crystalline fibres radiating from a centre, and the cause of the characteristic cross is easy to see. Because of the symmetry of the arrangement the light traversing the aggregate remains polarised in two planes, one containing the original vibration vector, and the other normal to it, while elsewhere it is, in general, elliptically polarised. Closer consideration shows that the cross should be accompanied by rings, for which, however, the law of spacing is different from that which holds for a uniaxial crystal, cut normal to the optic axis, examined in convergent light.⁵ With the minute spherulites seen in the films, the attainable resolution is too small to enable the rings to be distinguished. The spherulite need not necessarily be complete, but may consist of only a half sphere of radiating particles, with a diametrical plane on the surface, or of a wide angle cone, which could not be optically differentiated.

Prolonged heating at the temperatures named tended to increase the number of spherulitic centres of crystallisation, but not their size. From their much darker appearance than the background in ordinary transmitted light, it appears that they are much thicker than the rest of the film, and so must contain matter that was originally spread over a surrounding area. No light halo is, however, ever observed round the particles at this stage, from which we conclude that the matter is supplied from the surface layers of the film rather than from the whole thickness. The surface of the film is therefore mobile at temperatures about 700° C. below the melting point. Fig. 3 * shows part of a film which has been heated at 280° C. for 5 hours in all.

If a silver film is further heated at a higher temperature, round about 300° C., new spherulitic particles form, and the first ones show a slight growth of the black area; while raising the temperature by a further 10° or so causes firstly a rapid growth in size of the particles, and secondly the appearance of clear patches, of an irregular shape, which are particularly marked in the neighbourhood of large particles, and apparently indicate regions from which metal has flowed to a greater depth, to feed the growing centres. Fig. 4 * shows the appearance of the place represented in Fig. 3, * after a further heating for half-an-hour at 306° C. These patches, which we call "windows," do not represent bare glass, for, firstly, a scratch made across the film clearly removes metal from these regions, and, secondly, peculiarly enough, the windows scatter more light than either the rest of the film or the bare glass. They can just be distinguished in Fig. 4, * which is, of course, between crossed Nicols, but are better seen in Fig. 6, † which shows another film, heated to 345° C., by ordinary transmitted light.

The particles which have grown show a marked increase of dark area. As the crystal structure of gold and silver is cubic, a properly formed lattice should appear dark between crossed Nicols, and we must conclude that as the temperature is raised, the growing crystalline particle takes up the macroscopic ordering in the middle. With further heating, at temperatures up to 350° (still 600° C. below the melting-point),

⁵ See H. W. Morse and J. D. H. Donnay, *Spherulite Optics*, *Amer. Jour. Science*, 1932, **23**, 440.

* Plate XXXVI.

† Plate XXXVII.

the particles grow, and the larger of them take on a definite crystalline outline, and appear completely black except for a narrow region at the edge, which appears birefringent. Fig. 5 * shows the state of affairs after heating at 345° for 2 hours. The form of the outline is always that of an equilateral triangle, either complete, or with the corners cut off by lines parallel to the opposite sides, *i.e.*, the crystals are seated on (111) faces. It is to be emphasised that small spherulites may be found on films in this stage, but that invariably it is small particles, of the order of 1μ across, which show the characteristic cross, while large particles, of the order of 5 to 15μ across, show a well-defined crystalline outline and appear dark between crossed Nicols. All attempts to grow a large spherulite failed. Fig. 7 * shows a large crystal, of well-defined outline, with a background of small spherulites. The spherulite which appears in (actually on) the large crystal is due to a second deposition and heating, and illustrates the reluctance of the crystals, mentioned again later, to grow in a direction normal to a (111) face. Fig. 8 † shows similar crystals by ordinary transmitted light.

The film has now been considered up to a stage where extensive windows and a large crop of well formed crystals have appeared. Further heating, at round about 500°C ., produced a remarkable effect, a crop of very small crystallites appearing in the windows, which furnishes further proof that an exceedingly thin film of metal exists in these places. It appears from this that a higher temperature is needed to produce crystallisation in a film about 10 atoms thick than in one of a few times this thickness. This was confirmed directly by preparing a film about 8 atoms thick, with which centres of crystallisation were not obtained at temperatures lower than 420° , while a 50 atom film heated side by side gave them at 260° . The very thin film, with distinctive properties, existing in contact with a very much thicker layer in the ordinary windowed film, is reminiscent of the black spot existing, without gradual transition, alongside the very much thicker soap film. Heating to 600° produces a film which appears colourless to the eye, and turns out to consist of crystals at all stages of growth, from small spherulites to large, well-formed crystals, on a background of very thin film, the existence of which can be revealed by a scratch.

The sequence of changes described for silver films seems to be independent of the substrate. The fullest series of observations were obtained with quartz glass, but ordinary glass, the natural face of a diamond crystal and the fresh cleavage surface of mica, have all been used as substrate and, as far as the less complete experiments allow us to say, their behaviour was just the same. The behaviour of gold films is not sufficiently different to warrant a second detailed description. All the changes take place at somewhat (about 100°C .) higher temperatures.

It appears, then, that there are various stages of surface stability in these metal films. The most freely mobile part is the surface layer, which goes to form the first spherulite aggregates at the temperature at which they first appear. At a somewhat higher temperature, we have a very thin film, of the order of 10 atoms thick, as a stable state, anything between this and the full thickness of the film being unstable, as indicated by the windows. At a higher temperature still, the surface layers of the thin film became mobile, and allowed spherulites to be formed. The examination of this thin film, by the electron beam,

appears to be very desirable, and I hope to carry it out with an apparatus constructed on the lines described by Professor G. P. Thomson, which has just been completed.

In considering the formation of the spherulites, which are the earliest steps of crystallisation detected by us, we are met with the difficulty that we do not know if the original sputtered film is amorphous or crystalline. It is certainly amorphous to the highest microscopic resolution, but the electron beam indicates a crystalline structure in which the blocks are about 10 atoms across. We now come to the difficulty to which reference has already been made: how can we be sure that the electron beam has not, by heating the metal locally, produced a preliminary crystallisation? In Rupp's experiments with the electron beam the films were certainly heated during the examination, but in the experiments of G. P. Thomson and his co-workers,⁶ which establish the existence of minute crystallites, about 13 atoms across, in sputtered films, the extent of heating is uncertain. H. Kahler,⁷ who examined the structure of films, of unspecified thickness, by X-rays, says that films formed by evaporation show no structure, but that sputtered films show a crystalline structure. He took no precautions against heating, and it is our experience that, in the absence of special care, such heating, as evidenced by colour changes, always takes place. It seems pretty clear to-day that in sputtering the films are formed not, as Kahler thinks, by transport of crystalline lumps but by atomic deposition, so that there is no reason why unheated sputtered films should not be amorphous if evaporated films are. I believe, therefore, that there is no compelling evidence that films formed under our conditions have a microcrystalline structure, and that the point needs careful investigation.

Supposing that the film is amorphous, the formation of spherulites can be explained along the following lines. The first stage is the gathering together, by the motion of the surface layer to a depth of one or two atoms, of a small aggregate some few atoms across. It is clear that a very small collection of atoms cannot constitute a cubic lattice, but will form an approximately spherical aggregate. As this aggregate grows, local patches in which the array is approximately quadratic will form on the surface, and, from these, long fibres of cubic crystal, probably some ten atoms across, will grow out. A crystal in the form of a quadrangular prism ten atoms across and some hundreds of atoms long, cannot, however, maintain a strictly cubic array. Lennard-Jones has shown that in a plane lattice the spacing is wider than in a cubic lattice, if van der Waal's forces are operative between the atoms, so that in a crystal plane which is limited to, say, ten atoms in both directions, the spacing will almost certainly be greater than in a direction in which the crystal extends for hundreds of atoms. This would account for the uniaxial properties of fibres of a crystal that in the massive form adopts a strictly cubic lattice. If this argument is correct, it shows that extreme caution must be used in interpreting the broadening of electron diffraction lines in terms of limited crystal size—spacing effects, as well as diffraction effects, may play their part.

The contamination by mercury vapour, which took place in the early experiments, before special precautions were introduced, has effects which are of interest in connection with the first steps of crystallisation. The observations were mostly made on silver films. The

⁶ G. P. Thomson, Stuart and Murison, *Proc. Physic. Soc.*, 1933, 45, 381.

⁷ *Physic. Rev.*, 18, 210, 1921.

first indication of the presence of mercury is that the film shows yellow spots, of from 1μ to 80μ across. If the film is kept at atmospheric temperature it gradually becomes first redder and then more transparent. A variety of interesting effects have been observed, but that which concerns us here is that after a few days the film is covered with minute spherulites, of exactly the same appearance as those produced by heat. These spherulites increase in number with time, until eventually the film proves colourless. Fig. 9 * shows a portion of such a film four months after preparation, when the development of spherulites is very marked, between crossed Nicols. This is the state of affairs outside the originally contaminated spot: within the spot well formed, larger crystals are found, which are optically isotropic, except at the edge, just as were the crystals produced by heating at the higher temperatures. If a contaminated film is heated shortly after preparation, the yellow spots are converted into dense masses of spherulites.

It appears, therefore, that the effect of a minute trace of mercury is in some way to increase the mobility of the film, with the result that the first stage of crystallisation can take place at atmospheric temperature, and that this first stage is the formation of a spherulitic aggregate. A somewhat higher concentration of mercury leads eventually to the formation of isotropic cubic crystals, and so imitates the effect of higher temperatures. The very compact formation of spherulites which takes place when a contaminated spot is heated may be interpreted as showing that the mercury has so increased the mobility that the whole thickness of the gold film, and not merely the surface layers, is involved.

Since slow aggregation seems to lead to spherulitic formation, another method of producing aggregates was tried. Small gold particles, of the order of 1 or 2μ in diameter, were grown by slow reduction, first of all in silicic acid gel, and secondly in aqueous solution. In both cases the particles were found to show the optical behaviour typical of spherulites. Fig. 10 * shows such gold aggregates.

It appears, then, that when gold and silver atoms are brought together by any process of slow diffusion, the first stage of crystallisation is the formation of a spherulitic aggregate, in which the fibres, on account of their small transverse dimensions, have not the usual crystal spacing in directions normal to the axis, so that lattices which are cubic in the massive state may be optically anisotropic.

As regards the isotropic crystals formed at a later stage, in the case of films on a solid substrate these have a preferential orientation. In the experiments of Dr. Martindale and myself, where the films have been systematically heated up to 600° or so, the crystals always form with a (111) face parallel to the substrate, growing freely in a tangential direction, but adding atoms normally to the last completed (111) face only with great reluctance. We have shown, on the lines indicated by Kossel, in his considerations of crystal growth, that this is to be anticipated on energetic grounds. Other workers, notably G. P. Thomson, Stuart and Murison⁸ and S. Ramaswamy⁹ have found a preferential orientation on the (111) face, the former workers with platinum, and the latter with gold. Thomson, Stuart, and Murison, however, also obtained (100) as a preferred face, but they state that no attempt was made to investigate or control temperature conditions, so that it cannot be said that their results contradict ours. Ramaswamy first obtained

⁸ *Loc. cit.* ⁶

⁹ *Proc. Physic. Soc.*, 1934, **46**, 739.
* Plate XXXVIII.

orientation at 430° C., which agrees pretty well with our observations, and also observed growth with temperature. Dixit,¹⁰ working with thin evaporated films, heated to different temperatures, showed that the nature of the substrate did not affect the orientation; for the cubic metals silver and aluminium, the orientation was on the (111) plane at lower temperatures, although with silver at above 700° (outside our range) he also obtained (200) orientation, and with aluminium at 350° and higher he obtained orientation other than (111).

It seems definitely established, then, that with gold and silver up to temperatures of 800° and 700° respectively, the orientation is on the (111) face, whatever the substrate, although at higher temperatures this may be disturbed.

¹⁰ *Phil. Mag.*, 1933, **16**, 149.

GENERAL DISCUSSION.

Professor G. P. Thomson (*London*) said: I entirely agree with Professor Andrade that the electron diffraction and microscopic methods of examination are complementary and should both be used.

Professor L. S. Ornstein (*Utrecht*) said: The paper of Professor Andrade is certainly extremely important. It may be asked, however, whether his explanation of the stated facts is necessary.

Some evaporated gold layers of different thickness were shewn during the discussion; they shew colours which are in every respect analogous to those of colloidal gold-solutions with particles of different size. These colours may be explained in the same way as those of colloidal solutions by the theory of Gustav Mie, on the assumption that the optical properties of the particles are the same as those of solid gold. If this be so, it is hardly probable that the distortions assumed by Professor Andrade occur, for they would seriously affect the optical properties. It will therefore be necessary to look for another explanation of Andrade's polarisation effects. Now, the scattering of light is accompanied by polarisation, so that the combination of form and scattering could perhaps give rise to the observed phenomena.

Professor G. I. Finch (*London*) said: Certain precautions must be taken in preparing pure metal films by cathodic sputtering, and these have been fully gone into by Mr. Stuart, Dr. Ikin and myself.¹ I must say we did not find that heat alone affected the colour of a platinum or gold film—much depended upon the nature of the gas in which sputtering was carried out. When the pure metal is required it is advisable to sputter in argon maintained at a high degree of purity, though, under certain conditions of sputtering current and voltage, it is possible to obtain oxide-free films of gold, platinum and silver even in the presence of oxygen. When exploring the ground we used both water-cooled and un-cooled cathodes and receivers; but, in so far as experiments carried out at low rates of sputtering in argon were concerned, we found by electron diffraction and catalytic examination of the films that it was quite immaterial whether the films were deposited under water-cooling conditions or not. It may be remarked here that the test of catalytic activity and electrical condition of the sputtered surface afforded a far more sensitive basis of comparison

¹ *Proc. Roy. Soc.*, 1933, **A141**, 414; 1934, **A145**, 551.

between different films than the structural or optical properties (*i.e.* colour to transmitted light and texture of the surface as seen in reflected light). Microscopic examination with a Zeiss 2 mm. oil-immersion apochromat, in conjunction with a wide aperture achromatic oil-immersion condenser and correct tube-length adjustment, failed to reveal any signs of inhomogeneity in the sputtered films—an observation which agrees with that now made by Professor Andrade. Nevertheless, without exception, all such platinum, gold and silver films sputtered in argon were crystalline, the size of the crystals being, as a rule, larger the slower the rate of deposition and, incidentally, the lower the temperature of the receiver. Our first specimens were examined by Professor Thomson and Mr. C. A. Murison, and owing to bombardment by molecular rays during examination they frequently had a frosted streak on them where the electron beam had impinged. In our later work, however, where the electron beam had been freed from molecular rays, the electron diffraction examination had not the slightest observable effect upon the surface.

Professor Andrade suggests that the electron beam may produce heating effects sufficient to lead to crystallisation. I would point out, however, that the mean free path for ionisation of high speed electrons in a solid is of the order of 400 Å., whilst the effective specimen thickness in the case of electron diffraction is only of the order of 100 Å. or less. Finally, a film of paraffin wax of this order of thickness and melting at 45° C. yields an excellent single crystal pattern which remains unchanged virtually indefinitely, even when an electron beam carrying about 10 micro-amperes is being diffracted. It seems to me that the most convincing proof of the view that in sputtering as in evaporation, the films are formed by atomic deposition is afforded by the experiments of Finch and Quarrell² on the deposition of aluminium on platinum and by experiments cited in our present paper which illustrate the effect of the substrate upon the orientation of sputtered films. I think that we now have ample experimental evidence to show that sputtered films of pure metal are invariably crystalline, and in view of this, surely it is reasonable to conclude that the formation of the spherulites observed by Professor Andrade can best be regarded as the grouping of submicroscopic crystals into dendritic growths.

Dr. A. G. Quarrell (London) said: Professor Andrade quotes some results from a paper by Ramaswamy in support of his conclusion that gold and silver films take up (111) orientation upon heating; in the same paper, however, it is also shown that sputtered metal films are crystalline before heat-treatment. Surely Professor Andrade should give his reasons for not accepting this result if he is going to assume that sputtered films like evaporated metal films will be amorphous as far as X-rays can tell us. Quite apart from this, the structural examination of thin films by means of X-rays is very unsatisfactory, and Kahler's results cannot be accepted as evidence that thin films of evaporated metal are amorphous. It is our experience that all evaporated and sputtered metal films are crystalline even when the receiver is cold, and the discrepancy between the results of X-ray and electron diffraction methods is to be accounted for by the very much—at least one hundred times—greater resolving power to be obtained with electron diffraction.

² *Proc. Roy. Soc.*, 1933, **A** 141, 398.

Further, the statement that the orientation of the gold and silver films up to temperatures of 800° C. and 700° C. respectively is (111) whatever the substrate is hardly justified in view of the narrow range of substrates used. We have obtained a platinum film exhibiting no less than three distinct orientations simultaneously, although the temperature of the receiver certainly never exceeded about 50° C. Similarly, gold and silver films frequently exhibit (100) or (110) orientations, and it can be said quite definitely that the substrate plays a most important rôle in determining the orientation of the deposited film.

On the all-important matter of the nature of the gas in which sputtering was carried out Professor Andrade gives us no information, and, as silver easily gives an oxide and both silver and gold readily form interstitial solutions with oxygen during sputtering, I think it would be most helpful if Professor Andrade would give us more details about his sputtering conditions and tell us what steps he took to make sure he was dealing with pure silver and gold specimens. I may point out that a film of which the surface layers, at any rate, are silver oxide is optically indistinguishable from a silver film.

Dr. L. Tronstad (*Trondheim*) said: I share the doubts expressed by Professor Ornstein, whether the "double-refraction" observed at the edges of the metal crystals are due to internal anisotrophism. It is more likely that the bright edges, occurring between crossed Nicols, is due to reflected or scattered light. When the plane polarised from the polariser is reflected at the edge of the metal crystals, it is bound to be turned into elliptically polarised light (except in cases where the plane polarised light vibrates in the plane perpendicular to the plane of incidence), and such elliptically polarised light cannot be extinguished by the analyser.³

Professor V. Kohlschütter (*Bern*) communicated: The observations and interpretations made by Professor Andrade are of considerable interest in connection with the problem of "somatoid" elements in electrolytic deposits (which have been the subject of my own contribution) and the question of somatoids in general.

Professor Andrade assumes that the first products deposited from a metal-spray possess a definite structure, revealed by their behaviour in polarised light. If his assumptions are correct, these products must be considered as somatoids; moreover, they represent an especially simple case of somatoidal structure. Our previous experience teaches us that the formation of somatoids is always due to the presence of "auxiliary" substances in the state of colloidal dispersion. In the case discussed by Professor Andrade, no foreign matter is present in the spray; and the primary particles of the metallic deposit must themselves play the rôle of the "auxiliary" substance. Another feature of the case is, that the somatoids are considered to represent an *intermediary state* of aggregation of the highly-dispersed primary material, *preceding the formation of crystals*. They are thus supposed to play the rôle of *crystal-embryos*, in which they have never been observed before.

This caused me to ask Dr. K. Huber, after my return from London, to make some tests in my laboratory, using metallic films which were prepared more than twenty years ago under exactly controlled conditions,⁴ and carefully protected since against the action of the air. We repeated

³ Compare, for instance, L. Tronstad, *Z. techn. Physik*, 1932, **13**, 408.

⁴ V. Kohlschütter, A. Noll, *Z. f. Elektrochemie*, 1912, **11**, 419.

the experiments described by Professor Andrade with them, and found the same effects when observing a silver film, produced in pure hydrogen ($p_{H_2} = 0.25$ mm.) and thereafter heated to 200° . Beside fully developed crystals, in dendritic formations, we found elements analogous to those reported by Professor Andrade.

The microscopic examination aroused in us the doubts already expressed by Trönstad during the discussion in London. The four bright points which appear under crossed nicols instead of a single particle, may be due not to double-refraction, but to diffraction and reflexion as well. To test this point, Dr. Huber investigated particles of the same size, consisting either of finely powdered lead-sulphide or of sprayed mercury.

The photographs (Figs. 1-3)* prove clearly that *small homogeneous particles of an undoubtedly isotropic material* can have the same microscopic appearance as that observed by Professor Andrade. Observations of this kind can thus not be used as arguments for a spherulitic structure of the silver particles—i.e., as a proof of somatoid properties.

Dr. J. A. Darbyshire and Mr. E. R. Cooper (*Manchester*) (*communicated*): In connection with the thin metallic films, we would like to indicate very briefly some results we have obtained by electron diffraction methods at Manchester during the last few months.

We were continuing an examination of the oxide films removed from the surface of molten metal by the wire loop method⁵ using electrons of approximately 30 K.V. and working by the transmission method. We often obtained, in addition to the continuous rings due to oxide, quite extensive spot patterns due to the metal from which the oxide films had been removed. Fig. 4* shows a typical pattern from cadmium; the spots are due to cadmium metal and the continuous rings to cadmium oxide.

Recently we have been trying to find out something about the nature of the small crystal that could be responsible for such effects. If we take a photograph with the specimen fixed in position, we observe, on one plate, reflections from planes set at a considerably different angle relative to each other in the crystal lattice (that is, reflection patterns from planes belonging to zone axes inclined at a considerable angle to each other in the crystal lattice). This indicates the existence of a considerable amount of distortion, and apparently the patterns are due, not to a single crystal, but to a collection or aggregate of small crystallites set with a considerable degree of orientation so as to resemble, to some extent, a single crystal geometrically.

The distortion, or more correctly, the lack of orientation of the crystallites in these clusters is as much as 40 degrees in some cases. If distortion of this amount were to have taken place uniformly in all directions about the mean setting, we should expect the spots to be spread considerably around the arcs of the Debye Scherrer circles associated with the metal.

Actually, as may be seen from Fig. 4* the spots are remarkably sharp even when there is considerable distortion present. The distortion is estimated from the simultaneous occurrence of reflections from planes belonging to different zone axes in the crystal.

It appears that the reason for the sharpness of the spots is due to

⁵ J. A. Darbyshire and E. R. Cooper, *Trans. Faraday Soc.*, 1934, **30**, 1038.

* Plate XXXIX.

the existence of a well-marked fibre axis, lying in the plane of the film and normal to the direction of the incident beam. If there is a fibre axis like this it is possible for there to be a very considerable amount of distortion and yet for the spots to retain their sharpness.

Fig. 5 is a diagram of a pattern that we have obtained from cadmium (the rings are due to cadmium oxide). It is evident, from the geometrical arrangement of the spots, that there is a fibre axis along the line joining the $11\bar{2}0$ and $\bar{1}120$ reflections. Fig. 6 is a similar diagram for zinc indicating the presence of a fibre axis joining the $\bar{1}100$ and 1100 . We have drawn a ring around the reflection of type $2\bar{1}11$, $12\bar{1}1$ because they are forbidden by the structure factor for zinc. We have,

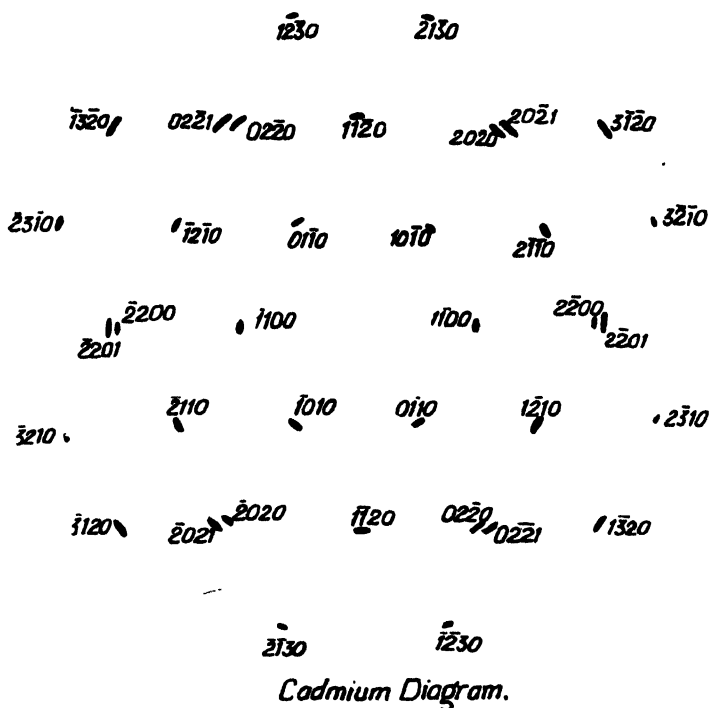


FIG. 5.

however, often observed reflections of this type and also forbidden reflections of type $30\bar{3}1$ from both zinc and cadmium, and we believe that we can account for these in terms of the distortion indicated by the geometrical arrangement of the spots on the plate.

Fig. 7* is a photograph of muscovite mica taken by the transmission method; in addition to the well-known hexagonal pattern, a number of other reflections can be seen lying along well-marked row lines joining up the principal spots of the pattern. This is apparently a case of fibre axis, not due to a bunching together of a number of smaller crystallites, but to a process of gradual curvature of a coherent and continuous film.

* Plate XL.

It is important to mention that we have found no definite evidence of any change from the normal spacing of these metals. Any such alteration must have been smaller than three quarters of 1 per cent.

Although in general the sharpness of the spots could be correlated with the existence of a fibre axis in the manner indicated above, nevertheless quite recently we have found some patterns from metallic bismuth in which the spots are sharper than would be expected from the existence of the fibre axis alone, and there appears to be still some other feature responsible for the sharpness of the spots.

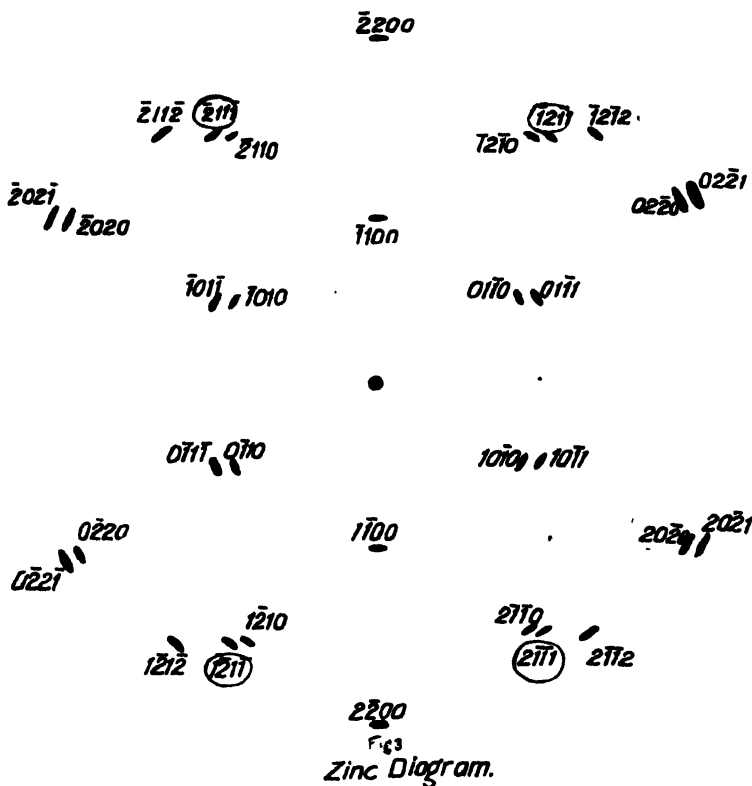


FIG. 6.

It is important to understand this in order to be able to interpret electron diffraction photographs in terms of orientation without ambiguity, and it is the object of our present researches to discover the nature of this additional effect which may be described as an apparent pseudo-fibre axis created by the directional effect of the incident beam whilst passing through the crystal. It is possible that there may be an interpretation in terms of the dynamical theory of electron diffraction.

Professor G. I. Finch said: If Dr. Darbyshire's Figs. 5 and 6 accurately reproduce the actual diffraction photographs, then it seems to me that the arcing of the spots indicates that he was not dealing with a single crystal but rather with an agglomeration of fairly well

orientated crystals, and that in the case of his Figs. 5 and 6 there are two such agglomerations though of different orientations. Compare, for example, our Fig. 46 in which two differently orientated single crystals of aluminium are in evidence. Dr. Quarrell and I have previously pointed out⁶ that diffraction of transmitted electrons does not normally distinguish between an array of perfectly orientated thin crystallites and a thin single crystal. If the orientation of the crystallites is not quite perfect, however, the spots are elongated into arcs. Thus, the phenomenon recorded by Dr. Darbyshire can be readily accounted for without postulating a "distorted" single crystal.

I seem to remember with Dr. Quarrell showing Dr. Darbyshire, at the Physical Society's Exhibition in January, 1935, the pattern Fig. 8* obtained from a flake of mica, and on that occasion, attributed the extension of the normal hexagonal pattern spots into rows to the fact that the very thin mica flake was bent about an axis roughly normal to the direction of this extension.

Professor E. N. da C. Andrade (in reply) said: As regards the criticisms of Professor Ornstein and Dr. Tronstad, it appears that while they find difficulty in accepting my explanation of the experimental effects, they have no alternative explanation to offer of the gradual transformation of the optical behaviour which takes place as the film is heated, *i.e.*, the transformation from the spherulitic figure to the complete blackness characteristic of a cubic structure between crossed Nicols. Dr. Tronstad's suggestion that the effect at the edge is due to elliptic polarisation accompanying reflection, offers certain difficulties. If the effect were due to reflection at the edges, it should apparently be marked with all crystals, but crystals are occasionally black between crossed Nicols, although in general they exhibit the double refraction at the edges shown in the photograph reproduced. Dr. Tronstad's suggestion is, however, one that will be borne in mind in future work.

I have carefully noted what Professor Finch says as to the colour of silver and gold films, and can only say that we certainly found, with our early gold films, changes of colour which could be completely explained by heating effects, and which disappeared when these effects were eliminated. As regards the crystalline state of the freshly prepared films, in the forthcoming publication, to which reference has been made,⁷ Dr. Martindale and I admit that it is quite possible that the unheated films consist of minute crystalline aggregates, as the following extract shows:

The electron diffraction results indicate that, in general, freshly prepared sputtered films consist of small crystalline aggregates with side lengths of a few unit cubes only. Since the films are inevitably heated to a certain extent during the process of examination, it is difficult to know if these very minute crystals are characteristic of the unheated metal films, but even if they should be, our picture does not need any essential modification. We have only to suppose that the spherulite is built up by an ordering of these very small blocks, whose size is less than the cross-section which we have postulated for our crystallite fibres, instead of by the ordering of single atoms.

⁶ *Proc. Physic. Soc.*, 1934, 46, 148.

⁷ *Philosophical Transactions of the Royal Society* (in the press).

* Plate XL.

I am afraid, however, that the train of argument on which Professor Finch relies for his proof that local heating cannot take place is too condensed to be convincing. At any rate I am not quite clear as to what process he has in mind. One way of looking at the matter is to consider the energy released when an electron is stopped in one act. A 30,000 volt electron has an energy of 5×10^{-8} ergs, while to raise a solid by 300° C. requires about 1.1×10^{-13} ergs per atom. The energy involved in the stoppage of one electron will therefore suffice to raise 5×10^5 atoms through 300° C., a number of atoms which constitutes a particle of about 50 unit cubes side length, which is certainly not less than the size of the crystallites contemplated by Professor Finch. Now if an electron encounters a nucleus it probably transfers its energy to it, and although the probability of such an encounter is small, it is quite large enough to give very many such encounters with the metal films and the electronic currents and densities used in the experiment. All that I wish to point out is that I do not think one can be quite sure that the electronic beam has no effect at all on the state of the film.

In reply to Dr. Quarrell, the films were prepared with air as the residual gas. The results obtained with gold and silver were essentially similar, and the probability of compounds forming between gold and the gas seems small. As regards the influence of the substrate, I was referring to non-metallic substrates only, where there is no resemblance between the crystal structure of the substrate and of the film. I am familiar with the work of Professor G. P. Thomson and his school on the influence of metallic substrates on the crystallisation of metal films.

The experiments described by Professor Kohlschütter certainly make it difficult to claim with any certainty that the aggregates in question are of a spherulitic nature, since the scattering and consequent polarisation of light from spherical mercury droplets gives a figure which imitates very closely that observed by Dr. Martindale and myself. At the same time it is to be expected that small fragments of cubic crystal, arranged at random, will give a different phenomenon, for unless the scattering or reflecting particle has circular or four-fold symmetry about the axis of the microscope, the intensity should be different in the four quadrants. Professor Kohlschütter's Fig. 1, taken with particles of galena, confirm this anticipation, for with the particle lowest in the picture one quadrant is completely missing and two others are imperfect.

This kind of thing was not observed with the initial particles in metal films, although in the case of colloidal gold particles, imperfect figures were occasionally, and deformed figures often, seen. I believe, therefore, that Professor Kohlschütter's photographs, while throwing grave doubt on the view that the figures are due to double refraction, confirm that there is a high degree of symmetry in the first gold particles formed when silver and gold films are heated. I propose, therefore, to call the particles which constitute the initial stage of crystallisation not "spherulites" but "spherulets," which leaves the question of double refraction open.

THE VALIDITY OF DRUDE'S OPTICAL METHOD OF INVESTIGATING TRANSPARENT FILMS ON METALS.

BY LEIF TRONSTAD (*Trondheim, Norway*).

Received 14th March, 1935.

It is known that the optical properties of a metal, as measured, for instance, by means of reflected polarised light, are largely influenced by optical density, by stress and by surface conditions; such measurements may therefore give valuable information about the properties of metallic surfaces. Since both the metallic coating and the underlying metal are usually covered with superficial reaction products (*e.g.*, oxide films), which may modify both the chemical and the external physical properties, the methods for studying such surface films are of special interest in connection with the present discussion.

The optical method of Drude based on the examination of polarised light reflected from the metallic surface, seems to be most suitable for the purpose, especially when combined with electron diffraction methods for investigation of structure. It has the advantage of permitting the study of the formation and changes of films, *in situ*, in prescribed environments but, naturally, at high temperature the amount of light emitted sets an upper limit to its applicability. A short review of the theoretical and experimental aspects, the fields of application and the results, especially those dealing with the normal and the passive oxide films on various metals, has previously been published by the present author in the Transactions of this Society.¹ Equations for calculation of the film properties from measured quantities were given, but the validity was not discussed in detail.

Theoretical Principles.

A short recapitulation of the principles of the method may not be out of place.

According to the electro-magnetic theory of light the optical properties of an isotropic absorbing medium (metal) are defined by two characteristic constants, namely the refractive index n and the absorption index κ . These constants can be determined experimentally, *e.g.*, by measuring the change in polarisation of the reflected light, which depends on the optical condition of the metal and the surrounding medium.

By resolving the electric vector of the incident polarised light into components I_p and I_v , respectively parallel and perpendicular to the plane of incidence, the state of polarisation may conveniently be defined by the phase difference and by the amplitude ratio of the two components. On reflexion at a metal mirror the two components are retarded in phase and reduced in amplitude to different extents. If δ_p and δ_v represent the retardation of I_v and I_p respectively, and R_v and R_p the amplitudes of the electric vectors after reflexion, the relative

¹ L. Tronstad, *Trans. Far. Soc.*, 1933, **29**, 502.

phase retardation Δ and the ratio of the absorption coefficients $\tan \psi$ are as follows :

$$\left. \begin{aligned} \Delta &= \delta_p - \delta_v \\ \tan \psi &= \frac{I_v}{R_v} / \frac{I_p}{R_p} \end{aligned} \right\} \quad . \quad . \quad . \quad (1)$$

Δ and ψ can be determined with great accuracy (± 0.01 - 0.02 centesimal degrees, i.e., $2\pi = 400^\circ$) by means of suitable experimental methods, which have been fully described in previous papers.²

The connection between the experimental Δ - and ψ -values and the optical constants of the clean metal is approximately (neglecting second order terms) given by the equations :

$$\left. \begin{aligned} n &= \frac{\sin \Phi \tan \Phi \cos 2\psi}{1 + \cos \Delta \sin 2\psi} \\ \kappa &= \sin \Delta \tan 2\psi \end{aligned} \right\} \quad . \quad . \quad . \quad (2)$$

Φ is the angle of incidence and it is essential to measure this angle with an accuracy corresponding to that of the Δ - and ψ -values. The equations are deduced from the law of refraction and the reflection formulæ of Fresnel, which demand, among other things, that the *surface of the metal should be optically sharp* with no transition layer at the surface.

In the presence of a surface layer, in which the optical properties change gradually from those of the surrounding medium to those of the bulk metal, the reflection formulæ are modified. The point was investigated theoretically by Drude, by considering the reflection at a surface covered with a number of intermediate thin films of uniform optical properties, and for the limit he found the influence of such a transition layer on the Δ - and ψ -values.

The equations obtained were complicated and cannot be applied to the experimental examination of surface films. But in presence of a uniform transparent isotropic film, *sufficiently thick* compared with the transition layers at the two interfaces between the film and the surrounding medium and between the film and the underlying metal, the equations can be considerably simplified. Thus, Drude has developed simple equations for metals covered with uniform films *in air*.³ These were later generalised for any surrounding medium by using the original theory of Drude. To the first approximation they may be written as follows² :

$$\left. \begin{aligned} \Delta - \bar{\Delta} &= -\frac{4\pi L}{\lambda} \cdot \frac{\cos \Phi \sin^2 \Phi}{(\cos^2 \Phi - n_0^2 a)^2 + n_0^4 a'^2} (n_1^2 - n_0^2) \cdot \\ &\quad \left[(\cos^2 \Phi - n_0^2 a) \left(\frac{1}{n_1^2} - a \right) + n_0^2 a'^2 \right], \\ 2\psi - 2\bar{\psi} &= \sin 2\bar{\psi} \frac{4\pi L}{\lambda} \cdot \frac{\cos \Phi \sin^2 \Phi}{(\cos^2 \Phi - n_0^2 a)^2 + n_0^4 a'^2} \cdot (n_1^2 - n_0^2) \cdot \\ &\quad \left[n_0^2 a' \left(\frac{1}{n_1^2} - a \right) - (\cos^2 \Phi - n_0^2 a) a' \right], \end{aligned} \right\} \quad (3)$$

where : $a = \frac{1 - \kappa^2}{n^2(1 + \kappa^2)^2}$ and $a' = \frac{2\kappa}{n^2(1 + \kappa^2)^2}$.

² Compare, L. Tronstad, *Det Kgl. Norske Videnskabers Selskabs Skrifter* (1931), No. 1, pp. 1-248; *J. Scien. Instr.*, 1934, 11, 144. The equations for evaluation of the Δ - and ψ -values are simply derived by spherical trigonometry, employing the method of Poincaré (cf. H. Poincaré, *Théorie Mathématique de la Lumière*, Vol. II. (1892), p. 275; L. Chaumont, *Ann. Physique*, 1915, 4, 103).

³ P. Drude, *Wied. Ann. Physik.*, 1889, 36, 532 and 865; *ibid.*, 1890, 39, 481.

Δ and ψ are the values obtained with metals in presence of a non-absorbing film of the thickness L and refractive index n_1 . $\bar{\Delta}$ and $\bar{\psi}$ are the corresponding values of the clean metal of refractive index n and absorption index κ , *free from any film*. Φ is the angle of incidence, λ the wavelength of the monochromatic light employed and n_0 is the refractive index of the transparent surrounding medium.

Clearly by measuring $\Delta - \bar{\Delta}$ and $\psi - \bar{\psi}$ under definite experimental conditions, both the thickness L and the refractive index n_1 of the film can be computed, and, thus, the equations provide an important means of studying thin transparent films on metal mirrors. From the equations, it can be concluded that the optical effect of the film is proportional to its thickness L and to the difference in refractive indices of the film and the surrounding medium. Thus, surface films of the same refractive index as the surrounding medium (*i.e.*, $n_1 = n_0$) do not affect the Δ - and ψ -values. For Φ about 60° , $\Delta - \bar{\Delta}$ is positive or negative, when $n_1 < n_0$ or $n_0 < n_1$ respectively. $\psi - \bar{\psi} = 0$ also when :

$$n_0^2 a' \left(\frac{1}{n_1^2} - a \right) = (\cos^2 \Phi - n_0^2 a) a'.$$

If the surrounding medium is a gas, then the refractive index n_0 is approximately equal to unity, and the above equations reduce to those of Drude. In that case the following explicit functions of the film-properties n_1 and L are obtained by division :

$$\left. \begin{aligned} n_1^2 &= \frac{1 + 2 \frac{\psi - \bar{\psi}}{\Delta - \bar{\Delta}} \cdot \frac{\cos^2 \Phi - a}{a' \cdot \sin 2\bar{\psi}}}{\cos^2 \Phi}, \\ L &= \frac{(\Delta - \bar{\Delta})\pi}{A \left(1 - \frac{1}{n_1^2} \right)^{200}}, \end{aligned} \right\} \quad \cdot \quad \cdot \quad \cdot \quad (4)$$

where :
$$A = -\frac{4\pi}{\lambda} \cdot \frac{\cos \Phi \sin^2 \Phi (\cos^2 \Phi - a)}{(\cos^2 \Phi - a)^2 + a'^2}.$$

Here $\Delta - \bar{\Delta}$ and $\psi - \bar{\psi}$ are measured in centesimal degrees. For green mercury light ($\lambda = 5460$ Å.U.) and iron with $n = 2.5$ and $\kappa = 1.4$ at $\Phi = 66.67^\circ$ in air these equations, for instance, become :

$$\left. \begin{aligned} n_1^2 &= 4.0 + \frac{30.0(\psi - \bar{\psi})}{(\Delta - \bar{\Delta}) \sin 2\bar{\psi}}, \\ L &= \div \frac{5.3(\Delta - \bar{\Delta})}{\left(1 - \frac{1}{n_1^2} \right)}. \end{aligned} \right\} \quad \cdot \quad \cdot \quad \cdot \quad (5)$$

The errors introduced in the equations by *neglecting second order terms* have been discussed by Drude and by the present author,² and such errors are very likely to be small compared with other sources of errors, for instance, from lack of homogeneity of films, roughness of the surfaces, etc. Thus, for an oxide film of 50 Å.U. thickness on iron, the error of the equations in the most unfavourable case should not be greater than ± 10 per cent. The influence of second order terms has also been examined by H. Hauschild,⁴ who found them negligible in all cases except

⁴ H. Hauschild, *Ann. Physik* (IV.), 1920, 10, 816; see also M. Blackmann, *Phil. Mag.*, 1934, 18, 262.

for silver, which has an extremely high absorption index ($\kappa = 19$ for green light).

Recently the problem of the effect of surface films on the reflected polarised light from metals has been analytically treated by C. Strachan⁵ for the case of orientated mono-molecular films. Whilst the theory of Drude treats the surface layer as a very thin volume distribution of matter and, thus, depends on the scattering of light by molecules in bulk, an attempt is made to find the effect of a "two-dimensional" assembly of scattering centres allowing for a *molecular orientation*. The equations obtained are similar to those of Drude and can be used for experimental determination of the scattering properties of groups of molecules in a "two-dimensional" state.⁶ The problem of anisotropic films has further been treated by applying the Maxwell equations for crystalline media in the same way as Drude applied the Maxwell equations for isotropic films. The same problem is also attacked in another way, namely by considering the layer as a three-dimensional distribution of oscillators according to the method developed by C. G. Darwin.⁷ These equations are all complicated but reduce to those of Drude for the case of isotropy, and this agreement may be taken as some evidence for the reliability of the simpler assumptions employed in the derivation of the equations given above.

Discussion of Errors.

In order to calculate the properties of a surface film by means of the equations given above, the $\bar{\Delta}$ - and $\bar{\psi}$ -values of the metal free from any film must be known. Under ordinary conditions the metals are covered with a thin invisible oxide film, formed in the presence of traces of oxygen, and, therefore, the true values can only be obtained when special precautions are taken to prevent oxidation or to remove the oxide film. H. Freundlich and collaborators⁸ found that the Δ -values of iron mirrors, formed from iron carbonyl vapour free from oxygen, decreased about 2° on admission of air, corresponding to the formation of an oxide film of about 10 Å.U. average thickness. The change could not be reversed at ordinary temperatures by evacuation. According to recent measurements in this laboratory,⁹ the Δ -values of polished iron mirrors in aqueous solution increased about 3-6° by removing the oxide film electrolytically in two different ways. Thus, the normal oxide films on iron are usually thicker (15-30 Å.U.) than found by Freundlich and collaborators and *cannot be considered to be mono-molecular* (in the sense of Langmuir) at low temperatures. However, on austenitic stainless steel the films are probably thinner, since here the films are usually less easily penetrated by oxygen. Several investigators have noted¹⁰ that it is also very difficult to obtain a perfectly clean mercury surface; fatty, water and/or oxide films of the same order of thickness as on iron are very easily formed. The thickness of the oxide films seemed to be largely affected by simultaneous presence of moisture and oxygen.¹¹

⁵ C. Strachan, *Proc. Cambr. Phil. Soc.*, 1933, **29**, 116.

⁶ C. G. P. Feachem and L. Tronstad, *Proc. Roy. Soc.*, 1934, **23A**, 127.

⁷ C. G. Darwin, *Trans. Cambr. Phil. Soc.*, 1924, **23**, 137.

⁸ H. Freundlich, G. Patscheke and H. Zocher, *Z. physikal. Chem.*, 1927, **128**, 321; 1927, **130**, 289.

⁹ L. Tronstad and T. Høverstad, *Z. physikal. Chem.*, 1934, **170A**, 172.

¹⁰ Compare L. Tronstad and C. G. P. Feachem, *Proc. Roy. Soc.*, 1934, **145A**, 115.

¹¹ See also L. Tronstad and T. Høverstad, *Trans. Far. Soc.*, 1934, **30**, 4.

For all exact optical work on surface films and in fact generally for all work dealing with external metal properties it is of paramount importance to determine the properties of the normal oxide films as well as to devise methods for removing such films. Therefore, it is planned to measure the true $\bar{\Delta}$ - and $\bar{\psi}$ -values directly on vacuum evaporated metal films. But since such films probably differ from bulk metal in grain size and solidity, as shown by electrical resistance, etc., and may not be free from internal stress,¹² it is also intended to measure cleavage surfaces of metal crystals in vacuo, and to remove the oxide films on polished metals with sufficiently easily reducible oxides by electrochemical reduction and hydrogen reduction or evaporation at higher temperatures. Immersion in liquids with the same refractive index as the surface films is also a method to be tested in order to get the values of the clean metal. Since the oxides have usually high refractive indices, attempts must then be made to replace the oxide film with a protective film of lower refractive index during the polishing process.

A further source of errors is introduced because the method assumes a *perfectly sharp change* between the different media. On mercury, for instance, the excursion of surface molecules due to thermal agitation gives rise to gradual change in optical density. A steady increase in the refractive index n_1 and a decrease in absorption index κ with decreasing Φ have been observed,¹⁰ and it is very probable that this is due to transition layer effect. Solid metals should be preferable in this respect, and reflecting surfaces may be obtainable by splitting single crystals with good cleavage, by condensation or by polishing. Drude has studied the formation of oxide films on cleavage faces of stibnite, galena and bismuth telluride, but it should also be possible to employ the same method for bismuth and antimony. Then the splitting should be performed in vacuo in order to avoid surface oxidation. Thin evaporated films are probably porous and microscopically rough, and may not be so suitable as polished metals. Although the mechanism of polishing is not quite settled, the presence of a deformed layer (Beilby layer) is very likely but, with care, optically reproducible results are readily obtained. In any case the best polished surface is certainly not plane, since the specific surfaces measured by various methods are greater than for the liquid. For metals with the best attainable polish (grinding on lead discs) the specific surface is at least twice as large as that directly measured. Assuming the increased surface to be due to polish scratches perpendicular to each other the effect would correspond to microscopical square pyramids with height $\sqrt{2}$ times the basal side.¹³

The effect of scratches and their orientation was originally studied by H. Fizeau¹⁴ and later both by Drude and the present author.² Scratches oriented at random were found to have a negligible effect on the Δ -values, whilst the ψ -values were reduced according to the number and size of the scratches. On polished metals, it was impossible to distinguish between different orientations of the polishing direction, and consequently the effect of scratches which are small compared with the wave-length of light can be neglected.

¹² That internal stresses (as well as impurities) largely affect the metal constants has been demonstrated by the present author with hard electrolytic nickel coatings, *Z. physikal Chem.*, 1929, **142A**, 241.

¹³ Compare, for instance, E. K. Rideal, *Surface Chemistry*, Cambridge, 1930 p. 175. See also G. P. Thomson, *Proc. Roy. Soc.*, 1931, **133A**, 1; *Phil. Mag.*, 1934, **18**, 640.

¹⁴ H. Fizeau, *Pogg. Ann. Physik.*, 1862, **116**, 478.

In an absorbing medium the incident and reflected ray penetrate about half a wave-length and, therefore, it is clear that all transition layers at the phase boundaries can affect the state of polarisation of the rays. But since the change is directly proportional to the thickness, it may be concluded that the effect of such layers is negligible provided that the uniform transparent surface film is relatively thick compared with the transition layers, although this aspect is not amenable to exact theoretical treatment.¹⁵ On the other hand, since the optical properties of a hypothetical Beilby layer must be somewhat similar to those of the underlying material, the effect must be much smaller than that of a surface film with different optical properties, even if such a Beilby layer is thick.

Another question to be considered is the *homogeneity of the film* itself. Heterogeneities in the films are easily detected during the observations (for instance, when the films are grown rather thick) by difficulties in getting sharp match. Clearly, therefore, quantitative investigations by the optical method are limited to films which are fairly uniform both in thickness and optical density. In other cases, the inhomogeneities of films (*e.g.*, films of fatty acids on mercury) may be studied conveniently by replacing the telescope of the polarisation instrument by a microscope focussed directly on the surface. Patches of different brightness can then be measured separately.¹⁶

For *thick homogeneous films*, for instance, of the order 200-400 Å.U., it is an open question whether the approximate equations hold good. H. Hauschild⁴ has shown that taking into account second order terms the state of polarisation of the reflected light is a periodic function of the film thickness, as a consequence of multiple reflection at both boundaries of the film. Thus it remains to be shown experimentally how far the simple equations given above can be employed. On aluminium in nitric acid, indication of such a periodic influence of the film thickness was found, but was tentatively explained in another way.¹⁷ Another effect to be considered in the case of semi-conducting films is the *absorption due to free electrons*, whose concentration may be modified for rectifying surfaces.

Internal stress in the film may cause double refraction, but for thin films this effect is probably negligible, since it is proportional to stress and thickness. Even for much thicker plates of glass the double refraction is comparatively small. However, since the incident light penetrates the metal to a depth of about half its wave-length, the effect of *stress in the metal* itself may be of a higher order.¹⁸ It is, therefore, desirable to avoid conditions which tend to the setting up of superficial stress, for instance, such as measuring films at temperatures differing from those of their formation.

Adsorbed gaseous films affect the Δ - and ψ -values of the metals in liquid media, since there the film and the liquid may differ much in optical properties. With metals in vacuo or in inactive gases, however, the effect of such films may be neglected, as the difference between the optical properties of thick films and surrounding medium is usually small.

¹⁵ J. H. Frazer, *Physic. Rev.*, 1929, **33**, 97, states that the transition layer on glass is about 40 Å.U., but does not appear to have considered the influence of possible stresses.

¹⁶ C. G. P. Feachem and L. Tronstad, *loc. cit.*⁶ See also L. Tronstad, *Z. techn. Physik.*, 1932, **13**, 408.

¹⁷ L. Tronstad and T. Höverstad, *Trans. Far. Soc.*, 1934, **30**, 362.

¹⁸ See also O. Lummer and K. Sorge, *Ann. Physik*, 1910, **31**, 325.

Experimental Confirmation.

It is clear that it is impossible to derive mathematical corrections for all the sources of error mentioned above. But the method undoubtedly possesses approximate accuracy for homogeneous films of medium thickness range (say 20-100 Å.U.) and of sufficiently different refractive indices. It is, therefore, of the utmost importance, for wider application of the method, to determine experimentally its actual limits.

P. Drude³ has already furnished qualitative information on the question by his measurements on cleavage faces; the changes of the optical properties indicated the formation of surface films by oxidation. The present author found the mean thickness of the passive oxide film on iron as anode in alkaline solution to be about 40 Å.U. with a mean refractive index somewhat greater than for ferric oxide in bulk. The thickness corresponded roughly to the coulombs passed through the surface, and further to the minimum thickness estimated by P. Krassa¹⁹ for similar cases, as well as with the thickness of PbO₂ and MnO₂ films on platinum, which K. Schreiber and A. Oberbeck found to give the superoxide potential.²⁰ Further, the law of growth of the oxide films on zinc found optically is the same as that found by other methods.¹⁷

Supporting evidence is also given by measurements of the optical effects of mono-molecular films of fatty acids on clean mercury.⁶ The thickness calculated for the most compressed state of the liquid film (area 22 Å.U.² per molecule) was systematically slightly greater than the chain-length, but the agreement was nevertheless striking as is to be seen from the table:—

Such orientated films are clearly not isotropic, but since the anisotropy is small, they fulfil the requirements of the equations to the first approximation.

Although the theoretical basis of the method seems sound and there is strong circumstantial evidence for its validity, it is still desirable to attempt direct experimental confirmation. Work along this line is now in progress in this laboratory. Further discussion of this point may be deferred until these new results are available.

	Chain-length in Å.U.	Calculated Film-thickness in Å.U.
Pelargonic acid	12	15
Lauric acid .	16	17
Myristic acid .	19	22

Fields of Application.

Fields of application are discussed in a previous paper to this Society,¹ but some new fields may be mentioned.

The greatest advantage of the optical method for studying the kinetics of film formation and change in gases or liquids, compared with gravimetric and gas-volumetric methods, is the small surface necessary, which facilitates the establishment of uniform experimental conditions. Further, the films can be studied *in situ* both at normal and elevated temperatures without affecting the process of growth.

¹⁹ L. Tronstad, *loc. cit.*¹ P. Krassa, *Z. Elektrochemie*, 1909, 15, 490, 981.

²⁰ K. Schreiber, *Wied. Ann. Physik.*, 1889, 36, 662; A. Oberbeck, *ibid.*, 1891, 42, 193.

The method should also be very suitable for determination of conditions of heterogeneous equilibria (decomposition of oxides, sulphides, etc.) and thus be adapted to several metallurgical problems.

In heterogeneous catalysis the technique may be of service for studying the mechanism, for instance, in the recent explanation (intermediate oxide) of the catalytic action of palladium in the hydrogen-oxygen reaction by D. L. Chapman and G. Gregory.²¹

Summary.

A short review of the optical method of Drude for examination of thin transparent films and of the assumptions on which the method is based, is given. The validity and applicability of the method for a wide range of surface problems are discussed.

The limitations are not yet thoroughly investigated, but considering the disadvantages of other methods for examination of thin surface films, the optical method deserves wider attention by investigators of surface problems.

The author wishes to express his thanks to A. B. Winterbottom for valuable discussion of the subject and to *Det Videnskabelige Forskningsfond av 1919* for grants.

*Institute of Applied Inorganic Chemistry,
The Technical University of Norway.*

²¹ D. L. Chapman and G. Gregory, *Proc. Roy. Soc.*, 1934, **147A**, 68.

OPTICAL RESEARCH ON EVAPORATED METAL LAYERS.

By L. S. ORNSTEIN (*Utrecht*).

Received 25th February, 1935.

Optical research on evaporated films of metals can give indications of the structure of the metal in thin layers and of the change of the layer by external agents. We can get films of metals in varying thickness by evaporation in vacuum from a tungsten wire heated by an electric current. Such films have been prepared in the Utrecht Physical Institute in connection with intensity measurements, as well as for the silvering of interferometer mirrors, and for the construction of thermocouples. They afford a very good material for research on the corrosion of metals, along which lines work is now proceeding in my institute.

For the investigation of thin films it is generally assumed that they form a compact plane layer, and in this paper we shall suppose this to be true to a first approximation. Veenemans has shown in his Utrecht Dissertation that the optical constants of an evaporated layer can only be determined by absorption measurements if layers of different but known thickness are used.

If a metallic layer of thickness d , refractive index n and absorption coefficient k , is evaporated on a non-absorbing substance (e.g. quartz) of

refractive index n' , it can be shown from the electromagnetic theory of light that a fraction given by the formula

$$\delta = 16n'(n^2 + k^2) :$$

$$e^{-\frac{2kd}{10}} \{ (n-1)^2 + k^2 \} \{ (n-n')^2 + k^2 \} + e^{\frac{2kd}{10}} \{ (n+1)^2 + k^2 \} \{ (n+n')^2 + k^2 \} \\ - 2 \left[\{ (n^2 + k^2)^2 - n^2(l + n'^2) + n'^2 - k^2(n'^2 + 4n' + 1) \} \cos \frac{2nd}{lc} \right. \\ \left. = 2k(n' + 1)(n^2 + k^2 - n') \sin \frac{2nd}{lc} \right]$$

is transmitted.

Now in this formula n' is a given function of the known wave-length $\lambda = lc$, therefore it must be possible to find k and n from absorption experiments if the transmissivity δ is measured for a series of values of d . Veenemans has given a very elegant solution for this complicated numerical problem.

The functions of n and k alone can be tabulated for given values of n and k ; for n' the value 1.5 can be assumed, as the metal has been evaporated on quartz; furthermore, those parts depending on $lc = \lambda$ and d can be tabulated for the values of the wave-length and the thickness of the layer used in the experiment. In this way the value of δ can be calculated at a given wave-length for values of n and k ($n =$

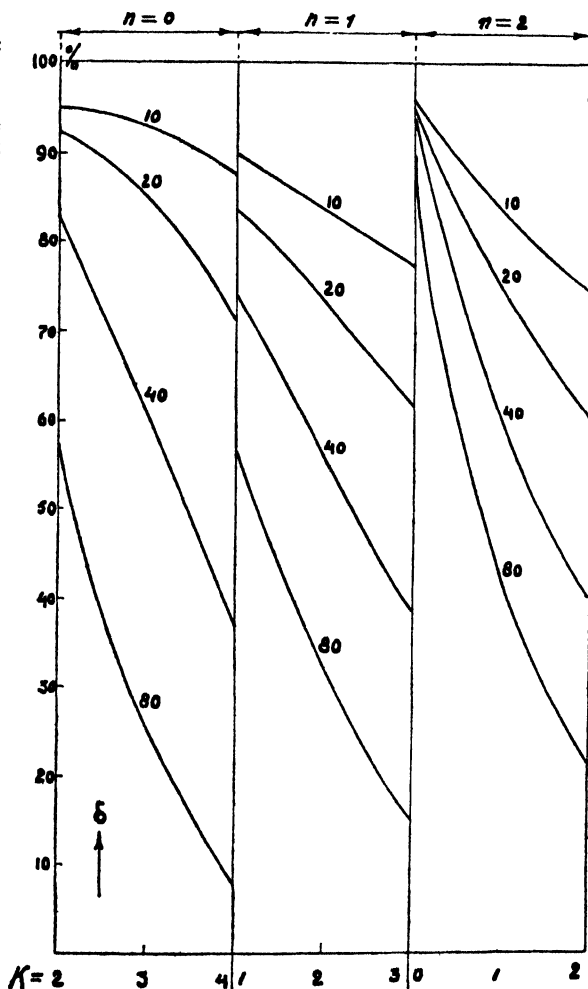


FIG. 1.

1.2 or 3, $k = 0.1, 0.2, 0.3, 0.4$) and the thickness d . These values can be

represented in graphs. Fig. 1 gives an example of the lines obtained in this way. From these graphs we can read off the values of n and k necessary to find the experimental value of δ for each thickness of the layer, and in this way we get a graphically determined relation between the quantities of k , n and d . If we plot, in a n - k diagram for the different values of the thickness of the layer, the relation between k and n , the curves representing the mentioned relationship in question ought to intersect in one point. The co-ordinates n and k of this point determine the quantities n and k for the wave-length under consideration. Fig. 2 represents this process for antimony at a wave-length of 15,000 Å. In Fig. 2 the experimental procedure used for the determination of the transmission δ can be any method for the measurement of absorption. In the work of Veenemans a monochromator combined with a thermopile to a galvanometer was used for the experiments in red and the near infra-red. Results for antimony attained in this way by Veenemans are

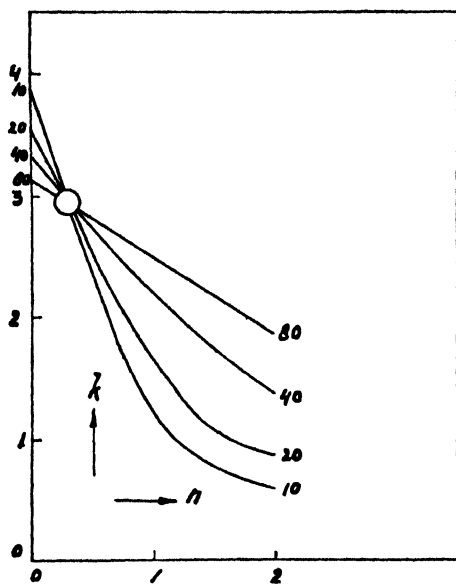


FIG. 2.

given in Fig. 3, where n is the refractive index, k the absorption coefficient, and k the absorption index.

The advantage of the method described in comparison with that of Drude consists in the fact that it can be used in the infra-red, and that it provides information not only as to the surface properties, but also as to the internal structure of the layer.

For visible light, the transmission can be determined very exactly with the spectral pyrometer. For layers of tin, silver, gold and copper this method of investigation has been used for various purposes. Chiefly for the investigation of the changes of thin metallic films the measurement of the transmission

is of great importance. This measurement can further indicate details about the constitution of thin layers. In Figs. 4, 5 and 6, we represent the measurements made on evaporated layers of gold of different thicknesses. The layer represented in (4) is the thinnest, it shows a red colour, a large transmission in the red, and again a specific transmission in the green. This great transmission in the red can be explained, if the larger part of the absorption is due to scattering of light by small particles. The layer (5) which is thicker, shows two marked minima of transmissivity which in my opinion should be explained as to that at 6400 Å by absorption, as to that at 5600 Å, perhaps more probably by interference in the thin layer, so that the layer shows a blue colour. The thickest layer which shows a green colour, has a transmission in the green and a marked absorption in the red; the properties approach to those of solid gold and in thick layers it has already a yellow metallic reflection. However, on observing the layers with the ultra-microscope,

one finds that they are in no sense plane layers, but seem to consist of small particles (crystals) either between thin layers or between a thin layer and the glass on which the layer is evaporated. Röntgenograms taken of thin layers of tin indicated that layers which are transparent to light showed no effect after a somewhat lengthy exposure. Layers prepared by evaporation (which are no longer transparent) show the Debye-Scherrer photographs of polycrystalline character. The evaporated layers therefore seem to consist of small crystalline nuclei which are formed by the condensation of the metal on the glass; and this condensation seems to take place in the first instance at random points. Afterwards, however, these atoms form centres of condensation at which the small crystals found for gold and tin are formed.

It seems that a combination of optical and Röntgen methods should be of considerable assistance in the investigation of thin films.

The transmission or the absorption of a film can be investigated in the manner described, thus giving a basis for further investigation; to the already-mentioned optical methods used for the measurement of the absorption there may be added the photographic method.¹

It may be of some importance to summarise a method used in the Utrecht Institute by Hamaker in order to determine the reflectivity of tungsten as function of the temperature. The method can be used for

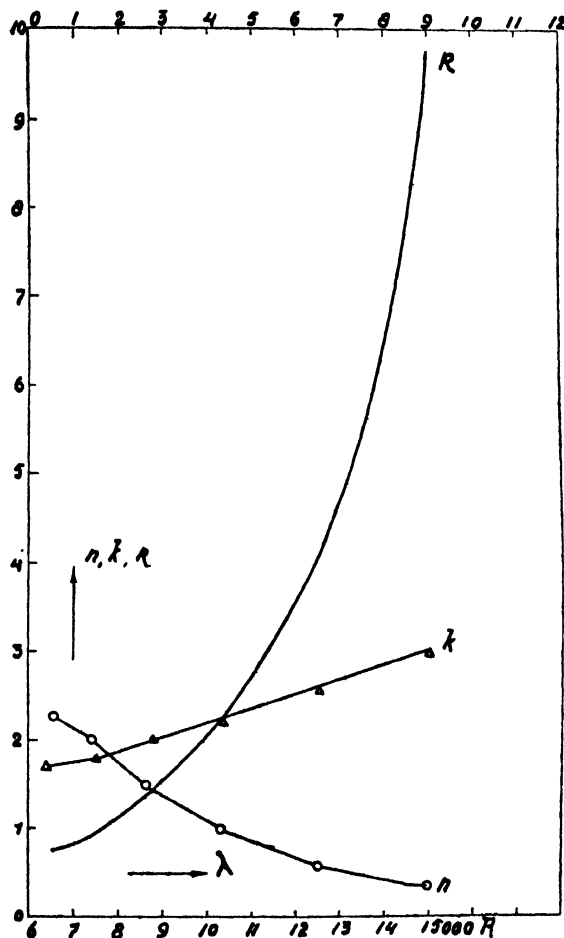


FIG. 3.

¹ Compare for full details: Ornstein, Moll and Burger, *Objektive Spektral-photometrie*, Vieweg Braunschweig, 1932. Ornstein, Eymers and Vermeulen: A visual spectroscopic method in heterochromatic photometry, *Proc. Amst.*, 1932, **35**, 278.

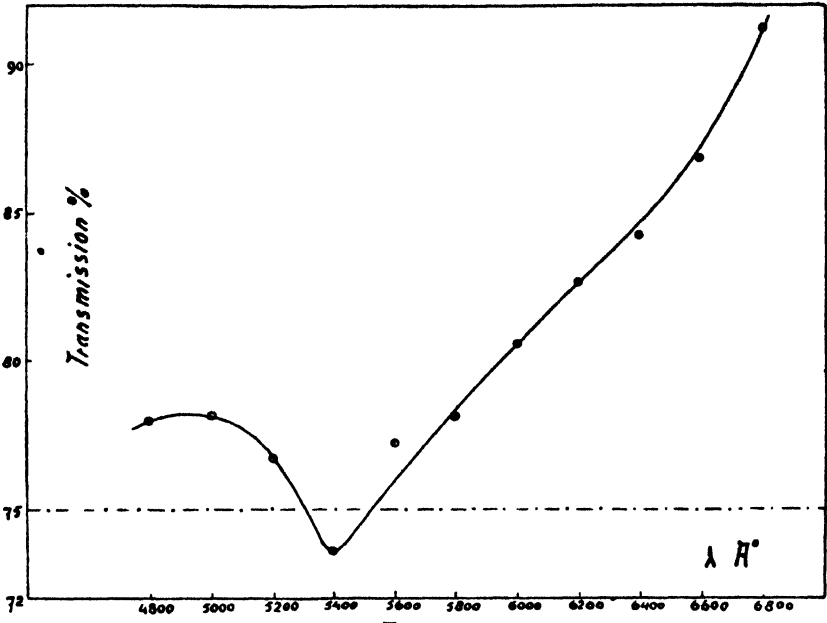


FIG. 4.

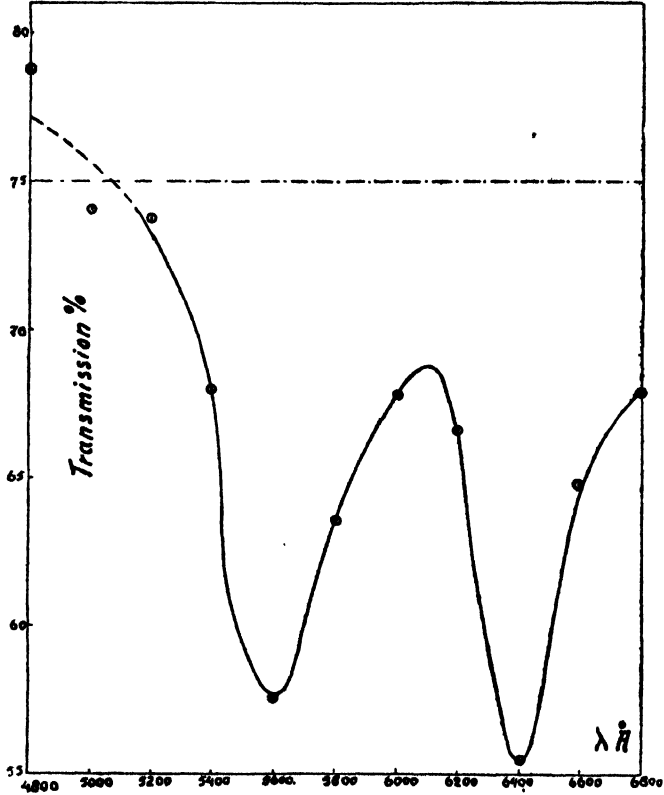


FIG. 5.

any metal or metal film deposited on another metal at different temperatures. The principle of the method is as follows:

The total reflectivity of a surface is defined as the ratio of the intensity of the total amount of light reflected to the intensity of the incident light.

We will put this definition into a more mathematical form. Suppose (Fig. 7) the intensity of the light incident along A on a unit of area and within a solid angle $d\Omega_A$ to be

$$I d\Omega_A,$$

then in another direction B and within a solid angle $d\Omega_B$ the amount

$$I d\Omega_A z_{AB} d\Omega_B$$

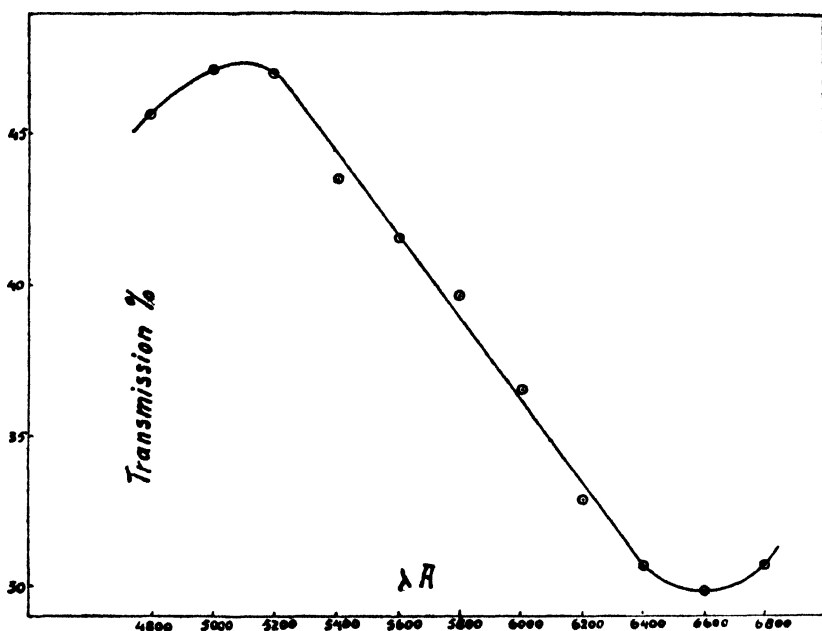


FIG. 6.

will be reflected; z_{AB} is the specific reflectivity from A to B. The total amount of light reflected by the unit of area will be

$$I d\Omega_A \int z_{AB} d\Omega_B,$$

where the integration has to be extended over a hemisphere, and consequently the total reflectivity for direction A is

$$z_A = \int z_{AB} d\Omega_B \quad (1)$$

The usual way in which z_A is determined by experiment consists of a practical application of formula 1, viz., of measuring the ratio of the sum of the intensities of the light reflected in different directions B to that of the incident light. In the following this method will be denoted as "the old method."

If the reflecting surface is curved, and if the reflection is partly diffuse and partly specular, z_{AB} will be an irregular function of the direction B, and it will therefore be almost impossible to arrive at accurate results

s'_A is the ratio with which the above theorem is concerned and which I will call the reflectivity for homogeneous illumination. But, since $z_{AB} = z_{BA}$, we have

$$s'_A = \int z_{BA} d\Omega_B = \int z_{AB} d\Omega_B = z_A \quad . \quad . \quad . \quad (3)$$

and the theorem is proved.

We thus arrive at a "new method" for the determination of a total reflectivity, *viz.*, by illuminating the surface homogeneously and measuring the reflected light in one direction only.

This new method has very great advantages compared with the old method; for the total reflectivity is now found in one single experiment, and the accuracy of the observations is entirely independent of the form and the condition of the surface. In using the old method we have, on the other hand, to carry out a whole series of experiments in each separate case, and when the reflection is very irregular, we can never expect to arrive at accurate results at all.

The investigations carried out on twelve strips of tungsten with widely different surfaces give full evidence of the value of the proposed new method; maximum and minimum of total reflectivity do not differ by more than 3 or 4 per cent.

The above reasoning applies also to a more general problem. Let a beam of light be incident on a piece of milk-glass, or on any other piece of turbid material. The light will then be partly transmitted, partly reflected, and partly scattered in all directions. The total fraction of the incident light that is not absorbed by the material can in this case again be represented by an integral as in formula 1

$$z_A = \int z_{AB} d\Omega_B,$$

where the integration is now to be extended over a whole sphere. And again, Helmholtz's law will give us an equation $z_{AB} = z_{BA}$, etc.

We thus arrive easily at the following generalisation of the theorem given above.

Theorem: If a piece of any material is illuminated homogeneously, the ratio of the intensity of the light leaving the material in a particular direction A to the intensity of the incident light is equal to $1 - a_A$, where a_A represents the total absorption for light incident along A.

Under homogeneous illumination, it is thus possible to measure the total absorption of any material in one single experiment. Special applications of this proposition have not been made in this paper, but I have given the theorem here, since its application may be of use to others.

We still have to investigate what errors will arise in the proposed experiments if the illumination is not perfectly homogeneous. In that case, we do not measure z_A as given by formula 3, but

$$z_A + dz_A = \int (1 + d_B) z_{AB} d\Omega_B,$$

where d_B represents the errors in the homogeneity of illumination.

The total error will consequently be given by

$$dz_A = \int d_B z_{AB} d\Omega_B.$$

The value of d_B can be determined by experiment for different directions B, and in most cases z_{BA} , or better, z_{AB} , may readily be roughly estimated from a preliminary experiment. Since we are dealing with a correction only, great accuracy is not necessary.

Finally, it must here be said that the method of determining total

reflectivity by homogeneous illumination has already been proposed in 1920 by Sharp and Little.³ These authors, however, did not give a sufficient proof of the general validity of the principle, and the method has not been used except by themselves.

The full description of the method is given in the thesis of Dr. Hamaker *Reflectivity and Emissivity of Tungsten*, with a description of a new method to determine the total reflectivity of any surface in a simple and accurate way. Utrecht, 1934.

The method is now in use for the investigation of the transition-points of metals. We have for this purpose constructed an incandescent lamp with a band of iron, this lamp is put in a photometric sphere and homogeneously illuminated by lamps put into the sphere. The reflection of the iron band is investigated as a function of wave-length with the help of photo-electric equipment, and the temperature of the strip is changed from value to value whilst currents of different values are passing. The temperature can be determined by pyrometric measurement with the spectral pyrometer, the reflectivity for each colour being known. In this way it is possible to determine with great exactitude the transition points which are shown by discontinuities within the scope of the temperature-reflectivity curve. It is possible to use the method for any material; for we can (by evaporation, scattering or any other method) cover tungsten strips with the material under consideration and so, passing a current through the tungsten, change the temperature up to about 3000 degrees if this is necessary and, as shown, determine the temperature of the surface from its emission, and the knowledge of the emission coefficient which follows from the experiment in the form indicated above. Investigations on this subject are going on in the Utrecht Institute, but it seemed to me that the method was of sufficient general interest to give the above indications of our manner of procedure. Working with alternating current, it is possible to determine from the temperature and the emission, which can be exactly measured, the specific heat of films as a function of temperature: a quantity which may be of somewhat considerable importance for our knowledge of their structure.

³ C. H. Sharp and W. F. Little: *Trans. Illumin. Eng. Soc.*, 1920, 802.

GENERAL DISCUSSION.

Dr. L. Tronstad (*Trondheim*) said: Professor Ornstein's entirely new optical method seems very useful for several purposes. It is, however, not quite certain that the optical constants of the evaporated porous metal films agree with those of the solid metal. I should, therefore, like to ask Professor Ornstein about the agreement between his metal constants and those of solid metals as determined by other methods.

Professor Ornstein also said that the method might be adapted for studying phase changes of metals at higher temperatures, which is a very important feature of the method from a metallurgical point of view. It is, however, not clear to me how far the emission of light from the metal layer at high temperatures interferes with the measurements and I should like to have Professor Ornstein's opinion on this point.

With respect to the corrosion experiments with the evaporated

films, which are referred to in the paper, conclusions about the service conditions of the corresponding solid metal can scarcely be drawn from the results.

Professor R. W. Ditchburn (*Dublin*) said: Let us consider the question of homogeneity of film. Homogeneity depends on our scale of measurement. Not even a single crystal is homogeneous if we make measurements on an atomic scale. The equations of Professor Ornstein and Professor Tronstad appear to be applicable when the film is homogeneous over distances of two or three wavelengths. I understand from Professor Finch that electron diffraction deals with properties averaged over distances of 0.1 mm. (area of 0.01 sq. mm.), though some degree of homogeneity over this area is needed to give clear pictures.

What are the conditions for producing homogeneity? Initially we should have (a) a uniform beam of boiled or sputtered molecules and (b) a uniform target. Condition (a) is easily satisfied, but recent work by Mr. Cox in my laboratory has shewn that it is extremely difficult to satisfy (b). A copper surface can in our experience be made uniform only by heating in vacuum nearly to melting, immediately before use.

An initially uniform film may be made non-uniform by surface motion as described in Professor Andrade's paper, but we should distinguish three kinds of surface motion. (a) Motion of sparsely distributed material over a substrate (see Cockcroft,¹ Esterman,² etc.) (b) Motion of atoms over a crystal of the same material (see Volmer,³ Adikari, etc). (c) Motion under quasi surface-tensional forces approaching liquid motion (see Professor Andrade's paper).

With regard to the question of the nature of sputtered films I should like to call attention to the work of Debinska.⁴ Does Professor Ornstein think that any of his results could be explained by the Maxwell-Garnett resonance colours?

Dr. L. Tronstad (*Trondheim*), in reply, said: Professor Ditchburn emphasises the question of heterogeneity of thin films. Thin sputtered metal films may not be considered as a homogeneous layer at all, as already mentioned previously in the discussion. Thin oxide films on solid metals are, however, entirely different, since they naturally have a tendency to "spread." Thus, thin oxide films (e.g., passive films) are usually fairly homogeneous in thickness, but their homogeneity is, of course, widely dependent on the properties of the base metal (inclusions, pores, etc.). The L - and n -values obtained from optical measurements are to be considered as approximate mean values of the films.

Professor L. S. Ornstein, in reply, said: The layers used are evaporated on glass which seems to be a uniform substrate. The idea suggests itself that the probability of condensation is rather small for the first atoms; that, however, when some atoms have been condensed, the probability gets larger for the newcomers to settle down on the condensed atoms. The number of elementary crystals found in the ultra-microscopical image (some are projected) seems not to differ very much in layers produced by different times of evaporation (or scattering).

¹ Cockcroft, *Proc. Roy. Soc.*, 1928, **119A**, 293.

² Esterman, *Z. Phys. Chem.*, 1923, **106**, 399.

³ Volmer, *Z. Physik*, 1925, **35**, 170.

⁴ Debinska, *Bul. Pol. Acad. Cracow*, 1930, **9-10A**, 460.

The accommodation of the atoms to the surface plays an important rôle. It would be possible to investigate this phenomenon somewhat more closely by optical methods, as has been done for Helium by van Wyk and Ornstein.

The Maxwell-Garnett resonance theory of the colours of thin layers seems to me less probable than the theory of Mie.

THE DETERMINATION OF THE STRUCTURE OF ELECTRO-DEPOSITS BY METALLURGICAL METHODS.†

BY D. J. MACNAUGHTAN * AND A. W. HOTHERSALL.†

Received 19th February, 1935.

Introduction.

The surface appearance of an electrodeposited coating frequently provides an approximate indication of its microstructure. Thus, deposits of a coarse columnar structure are in general visibly crystalline. When the microstructure is somewhat more refined, the crystal facets are smaller and less readily recognisable, but, due to scattering of light, the deposit has a typical matt appearance. The surface of deposits of a still finer grain has a smooth appearance, and when the grains are so small as not to be resolvable, or only just resolvable, under the microscope, the deposit usually has a lustrous appearance.

This surface appearance may be misleading. For example, a matt appearance which might be regarded as indicative of a structure composed of medium-sized grains, is sometimes due to the scattering of light by numerous rounded aggregates of microscopical dimensions. The matt, "frosted" or "milky" appearance of certain chromium deposits has been shown by Portevin and Cymboliste¹ to be due to this cause. Yet the microstructure of this type of deposit is too fine to be resolved with ordinary magnifications (say up to $\times 750$). Similar examples of a matt appearance due to minute rounded growths on the surface of a silver deposit of very fine grain size have been noticed by the authors. Again, in copper deposition from the acid sulphate solution, smooth deposits of non-crystalline appearance suggesting a fine structure but actually having a coarsely crystalline structure can be produced under certain conditions, whilst under other conditions a rough deposit, due to the formation of nodular outgrowths of fine grains, is obtained. Further, as shown in an accompanying paper by one of us (A. W. H.), the macrostructure of the basis metal is sometimes clearly visible after coating with an electrodeposit, although the microstructure of the deposit is found to be typically fibrous and not a clear continuation of that of the base.

It is thus evident that deductions as to the microstructure of an electrodeposited metal which are based entirely upon the surface appearance are liable to be erroneous. The true microstructure can only be determined by the usual processes of polishing and etching.

† Communication from the Research Department, Woolwich.

* Director, International Tin Research and Development Council.

† Research Department, Woolwich.

¹ *Rev. de Mét.*, 1933, 30, 323.

Previous to the work of Hughes, very little investigation of the microstructure of electrodeposited metals is recorded. Hughes attempted a systematic study of the microstructure of iron deposits and his work stimulated interest generally in this method of examination. However, the value of Hughes' work and of contemporary and previous work is now known to be limited by a number of considerations which were not apparent at that time, particularly when attempts were made to correlate the observed structure with the conditions of deposition.

Firstly, the important, and sometimes controlling, influence of traces of impurity in the depositing solution was not realised, and this led to the growth of erroneous conceptions. For example, until recently it was generally thought that the degree of fineness of the microstructure of nickel deposits increased with increase in the acidity of the solution. The opposite conclusion is now established and the prevalence of the earlier view would appear to have been largely due to the unsuspected influence of traces of impurity (probably of organic origin) in the solution. Similar marked effects on the characteristics of copper deposits are produced by minute concentrations of certain organic substances; for example, one part of peptone per million of solution is sufficient to cause a very pronounced reduction in the grain size of electrodeposited copper, and similar effects may be caused by contact of the solution, during preparation or use, with a wide variety of materials such as textile fabrics, rubber, etc.

Secondly, only inadequate and somewhat crude methods for the determination of the hydrogen ion concentration of solutions had been applied to the control of electro-depositing solutions and, as a consequence, the significance of such control, which is now known to be of very special importance in influencing the structure of deposits of metals of the iron group, was not appreciated.

Thirdly, the necessity for some quantitative method of testing electrodeposits to supplement the broad indications provided by examination of the microstructure had not become apparent.

In the last decade, experimental technique has advanced sufficiently to render possible a fuller insight into the structure of deposits and the factors which determine it. Improved methods have been adopted for controlling the composition of the depositing solution, amongst which probably the most important has been the development and use of methods for determining p_H . Also there has been an increased use of reliable methods for determining the cathode potential during deposition; while various devices for observing and measuring the stress in a deposit during deposition have been evolved and employed by a number of investigators. The examination of the deposit by means of the microscope has become more widely adopted, and in recent years has been supplemented by X-ray examination.

Consequent upon the accumulation of more precise data than was previously available, by the application of these methods attempts have been made to establish certain basic generalisations relating the structure to the conditions of deposition. It appeared at one time that it might be possible to co-ordinate all the factors involved in the deposition process in a manner first suggested by Bancroft in his well-known axioms which implied a definite relationship between crystal size and cathode potential. But in investigations of the metals of the iron group, particularly nickel, it has been found that, while the results of cathode potential measurements are invaluable as a guide to general changes in

the cathode process, they do not appear to bear any direct relationship to the structure of the deposit.^{2, 3}

Attempts have also been made to explain the variations in structure of deposits of these metals in terms of the amount of hydrogen that is co-deposited. The most comprehensive efforts in this direction have been based on observations that variation in the stress of the deposit was related to the amount of hydrogen discharged. It was assumed that the structure was related to stress and on this basis a dependence of structure upon the amount of co-deposited hydrogen was suggested. In this work, however, there appears to have been no direct examination of the microstructure of the deposits. It has been found subsequently, that the interpretation of stress measurements without reference to the microstructure is liable to error, since the stress may be relieved by the formation of cracks, so that a highly stressed deposit may yield a low stress result. Fig. 1,* for example, shows the surface appearance of a highly stressed nickel deposit, 0.012 mm. thick, which produced negligible bending of the thin metal strip on one side of which it was deposited. Taking suitable precautions to exclude such anomalies, no direct relationship has been found between stress in the deposits and crystal size,² which was the basis of the generalisation.

It appeared to the authors some years ago that, as the product of deposition is a metal, a careful examination such as is usually applied by metallurgists in the investigation of the structure of a metal, might throw additional light on the factors that influence structure of electro-deposits, provided the data acquired is related to known conditions of deposition. The extension of the methods of investigation to provide a more adequate metallurgical examination of the deposit involved supplementing microscopic and X-ray examination by reliable physical tests, and the application of these methods of examination to the deposit after it had been subjected to heat treatment. It has only been possible to carry out a portion of this programme even in the case of one metal only, namely, nickel, but the results appear to indicate the value of the methods employed, and suggest that they could be applied with advantage to other electrodeposited metals.

Physical Tests of the Deposit.

The Brinell hardness test was selected as being most easily applied to an electrodeposited coating and the results obtained have confirmed the value of this method. Correlation of the hardness figures with microstructure has shown that for any one metal there is a definite relationship, the hardness increasing with diminution in grain size. A series of nickel deposits of increasing hardness is shown in Figs. 2-6.† As the grain size decreases, it is clear that interpretation of the microstructure becomes increasingly more difficult and with the finer grained deposits large changes in hardness are found without any considerable change in microstructure. This is even more pronounced with chromium deposits, no marked difference in microstructure being apparent between the bright type of chromium deposit, with a diamond pyramid hardness (D.P.H.) of about 900, and the dull grey variety, with a D.P.H. of 500-600.

² D. J. Macnaughtan and A. W. Hotherhall, *Trans. Faraday Soc.*, 1928, **24**, 387.

³ D. J. Macnaughtan and R. A. F. Hammond, *Trans. Faraday Soc.*, 1931, **27**,

* Plate XLI.

† Plates XLI. and XLII.

Thus a quantitative method of determining the properties of electro-deposited metals, such as is provided by a hardness test, appears to be essential for supplementing the general indications given by the micro-structure, especially as the latter is inadequate for the study of fine-grained deposits.

Determination of the Hardness of Electrodeposited Metals.

The methods that have been developed for testing the hardness of metals may be broadly classified into two groups: (1) Indentation tests (in which the surface of the metal is permanently deformed by the pressure of another body), (2) Wear or abrasion tests.

Wear tests are difficult to standardise, and are in general only suitable for simulating particular conditions of service. It has, however, proved possible to standardise a number of indentation tests. Two forms of indentation test have been used for determining the hardness of electro-deposited metals—the ball or diamond indentation test and the scratch test which, as frequently applied to metals, is a form of indentation test, since the scratch is produced by flowing the metal rather than abrading it.

There are, however, a number of disadvantages attendant on the use of the scratch test which may be summarised as follows: (1) difficulty of obtaining comparable results with different instruments (2) the slight change in width of scratch for large differences in hardness, (3) (with an angular scratching point) wear and damage to the cutting edges with use, necessitating frequent standardisation for reproducibility and comparable results, (4) lack, at present, of precise information on the thickness of deposit required to eliminate the effect of the underlying metal. O'Neill found that his instrument, employing a hemispherical diamond scratching point, was only suitable for testing deposits over a limited range of hardness.

The Brinell hardness test is not liable to appreciable instrument error, and although it is necessary to deposit comparatively thick coatings, the advantages of accuracy and reproducibility which are obtained cannot, so far as the authors are aware, be given by any more simple procedure.

In very hard deposits, such as those of chromium, for which the Brinell test using a steel ball is unsuitable, the diamond indentation test may be adopted. The authors consider this test to be slightly less suitable for general purposes, owing to the somewhat greater thickness of deposit which must be applied (for an equivalent load) to eliminate interference from the basis metal. An advantage of the diamond pyramid hardness test is that the results are independent of load and hence the test can be applied to very thin coatings by the use of light loads. Difficulties of technique and interpretation of results, however, are experienced; thus the extent of surface hardening effects produced by polishing is uncertain and the small size of the impression obtained with light loads involves careful preparation of the specimen and a refined method of measurement; wear or damage to the diamond point also becomes of more importance as the load is reduced.

For testing deposits having a Brinell hardness number of 100-400, a 1 mm. ball and 10 Kg. load have been used. This necessitates a minimum thickness of deposit of about 0.01 inch for the softer of these deposits in order to avoid any interfering action of the basis metal. For accurate and reproducible results, the thickness of the softer, more coarsely crystalline deposits requires to be standardised, since the grain size tends to become larger with increasing thickness (owing to lateral growth of favourably placed grains). For this reason, the authors have adopted a standard thickness (after grinding and polishing) of approximately 0.01 inch for nickel deposits. Although this thickness is probably adequate to eliminate any possible effect of the underlying metal, even with the softest deposit so far obtained (Brinell number 125), the additional precautions are taken,

of using mild steel, having a hardness similar to that of the softest deposits, as a basis metal, and of using cleaning methods designed to produce a highly adherent coating. Rod of hexagonal section has been found to be the most convenient material for use as cathodes.

The application of thick deposits involves the necessity for careful control of the deposition process. In addition to the control of p_H , temperature, etc., precautions must be taken in the initial preparation of the solutions and anodes, by using specially purified salts and avoiding contact of the solutions with organic materials; and care must be taken to exclude foreign matter such as dust.

Hardness and Microstructure of Various Electrodeposited Metals.

The Brinell hardness test is clearly unsuitable for the examination of thin decorative coatings, and it has been primarily used by the authors in laboratory work to investigate the deposition process. No extensive investigation has been made to correlate the results obtained with thick deposits with the properties of thin coatings, but tests by O'Neill,⁴ using a hemispherical diamond scratching point, have indicated that the hardness of thin deposits bears the same relation to the conditions of deposition as the results obtained by the authors with thick deposits. A similar general relation has been found between Sanigar's scratch hardness results for thin silver deposits (using an angular diamond scratching point) and the authors' Brinell tests on thick deposits.⁵

Table I. shows the results of the application of the methods outlined above to various electrodeposited metals. These results show that, with most electrodeposited metals, considerable variations in structure and properties are possible, and that with some deposits, especially those with which hydrogen is co-deposited, the lowest hardness obtained is in excess of that of the metal when fully annealed. The magnitude of these effects,

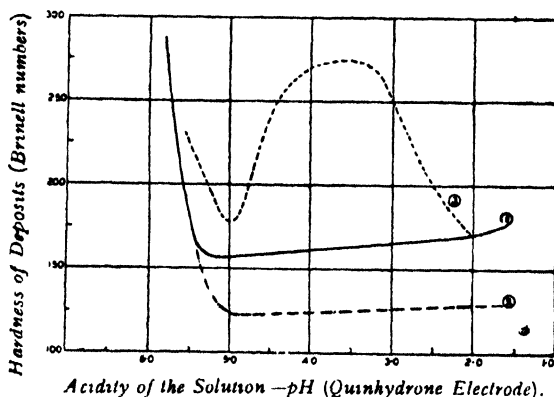


FIG.—7. Effect of p_H on the hardness of deposits.

Curve 1.—Solution contained nickel sulphate, boric acid and potassium chloride.

Curve 2.—Same as 1, but with nickel chloride instead of potassium chloride

Curve 3.—Same as 1, but without potassium chloride.

results obtained are briefly summarised below.

⁴ *Trans. Faraday Soc.*, 1931, **27**, 41.

⁵ D. J. Macnaughtan and A. W. Hotherhall, *J. Electrodepos. Tech. Soc.*, 1930, **5**, 63.

as indicated in the table, is sometimes considerably greater than can be secured by cold deformation of the pure metal.

Determination of the causes of these phenomena involves a careful study of the effect of conditions of deposition on the characteristics of the deposit, for which the methods already described appear particularly suitable. Such a study has so far only been carried out with nickel deposits and the

TABLE I.—HARDNESS AND MICROSTRUCTURE OF ELECTRODEPOSITED METALS.

Metal.	Solution.	Range of Characteristics so far Determined.		Factor Chiefly Responsible for Variation Observed.	Brinell Hardness.	
		Brinell or Diamond Pyramid Hardness.	Microstructure.		Of Fully Annealed Metal.	Of Work-hardened Metal.
Chromium	Chromic acid	400-950	No definite structure	Temperature, current density	70	—
Platinum *		606-642	Not available	—	47	97
Rhodium *		594-641	" "	—	101	—
Palladium*		190-196 385-435	" "	—	49	109
Nickel	Sulphate with addns. of various salts	125-420	Soft deposits—columnar crystals	p_H	70	300*
	With addn. of organic colloids	Up to 550	Hard deposits—no definite structure	Presence of colloids	—	—
Cobalt	Sulphate with addns. of various salts	164-380	Similar to nickel for equal hardness	p_H	86	—
Iron.	Sulphate chloride	140-350	Similar to nickel for equal hardness	Acidity and C.D.	69	148
Copper	Acid sulphate	40-62	Columnar crystals—large in soft deposits—finer or twinned in harder deposits.	H_2SO_4 concn.	40	102
	With colloids	Up to 130	Fine fibrous structure	Presence of colloids	—	—
	Cyanide	130-160	No definite structure	—	—	—
	Neutral nitrate with ammonium	300	No definite structure	—	—	—
Silver	Cyanide	60-79	Not available	Nature of added anion	25*	68*
	Cyanide with colloid	130	Not available	Presence of colloid	—	—
Cadmium	Cyanide	12-22	Not available	—	20	34 (Forged)
	Cyanide with, colloid	53	Fine fibrous structure	Presence of colloid	—	—
Zinc	Sulphate	40-50	Not available	—	33-40	52
Tin	Sodium stannate	8-9	Indefinite broken structure—coarse columnar crystals	Temperature	4-5	—

* R. H. Atkinson and A. R. Raper, *J. Electro-depos. Tech. Soc.*, 1934, 9, 77.

Properties of Nickel Deposits.

Hardness and Microstructure.

The most significant feature of the results obtained was the effect of solution p_H . Curves for various solutions, showing the changes in hardness with p_H are given in Fig. 7. In addition to the effect of p_H , the curves illustrate the previously unsuspected influence of alkali metal cations (*cf.* curves 1 and 2) and of the effect of the chloride ion (*cf.* curves 3 and 2).

Cathode Potential.

A notable feature of the results was the absence of any definite relationship between cathode potential and hardness or microstructure. In a given solution, for example, no marked change in cathode potential (>0.04 volt) was found over a wide range of solution p_H , corresponding to a considerable change in hardness. Furthermore, comparison of cathode potential/current density curves obtained in various solutions using similar conditions of deposition did not enable any consistent correlation with hardness results to be made.

Hydrogen Discharge.

Measurements of cathode efficiency were assumed to indicate the proportion of hydrogen discharged in relation to nickel. It was found that over a range of solution p_H in which considerable changes in hardness were found, there was no appreciable change in cathode efficiency. This suggests that co-deposited hydrogen does not exert a controlling influence in modifying the structure of the deposit.

Stress.

Preliminary results of stress measurements, using both the double strip method,² and a method of observing the movement during deposition of a magnified image of a strip, have failed to reveal any considerable change in stress to correspond with the marked changes in hardness and microstructure which takes place. On the other hand, the stress appeared to vary in a similar manner to the rate of hydrogen discharge.

Cause of the Hardness of Nickel Deposits.

The relationship between hardness and solution p_H which has been established suggested² that the cause of the high hardness and small grain size obtained at high solution p_H values was the interference with crystal growth exerted by colloidal basic nickel compounds which, due to the discharge of hydrogen ions, are precipitated in the film of solution surrounding the cathode. The effect of alkali metal ions in hardening and chloride ions in softening the deposit could then be explained by the influence of these ions in stabilising or flocculating the colloidal nickel compounds. Thus potassium, which helps to stabilise the material in the colloidal condition, tends to harden the deposit whilst chloride, which exerts a flocculating action, tends to soften the deposit. It is not at present established whether the hardness is controlled entirely by grain size or whether, as has been suggested by Desch, it may also be affected by the presence of the non-metallic particles in a critical state of dispersion.

These suggestions imply the presence of basic nickel compounds, nickel hydroxide or of oxide in the deposit and their substantiation demanded a method of establishing this.

Chemical analysis proved insufficiently delicate, and the most promising method investigated was the determination of the behaviour of the deposits on annealing.

² D. J. Macnaughtan, G. E. Gardam and R. A. F. Hammond, *Trans. Faraday Soc.*, 1933, **29**, 729.

The Effect of Annealing Nickel Deposits.

1. High Temperature Treatment.

The success of this method of examination as a means of revealing the presence of non-metallic solid material in electrodeposited nickel depends on conditions being favourable to grain growth or recrystallisation, so that the presence of non-metallic matter will be revealed either by reason of its segregation into amounts that are visible in grain boundaries and can be qualitatively estimated, or by its interfering effect on grain growth or recrystallisation. It is clear that the effect of annealing will be modified if the metal possesses any appreciable solid solubility for the foreign matter, and also that results may be negative if the deposit is free from stress, when little or no grain growth might conceivably take place even in the absence of interference.

Nickel deposits have, however, been found⁷ to give positive results in treatment for four hours at 1000° C. in vacuo, in good agreement with the indications provided by the hardness and microstructure of the metal as deposited. Thus, under the conditions used, all the deposits were stressed and grain growth was observed on annealing except with the hardest deposit examined. The softest deposits recrystallised giving large equiaxial grains with clean boundaries. With harder deposits having a well-oriented microstructure, grain growth took place chiefly in a direction at right angles to the plane of the deposit, lateral grain growth being relatively slight, due to the segregation of non-metallic material to the boundaries (Fig. 8*); this produced planes of weakness in the deposit which was thereby seriously embrittled, fracture taking place with very slight bending. With the hard deposits, having a fine grain size not well-oriented, small equiaxial grains were formed with boundaries containing globular material (Fig. 9*).

In view of the fact that all the deposits referred to above were prepared under conditions in which only traces of impurity were present, the non-metallic matter found would appear to be oxide, possibly contaminated with some basic material.

Application to Other Deposited Metals.

Only isolated attempts have so far been made to apply this technique to a study of other electrodeposits.

Coarsely crystalline tin deposits prepared in pure sodium stannate solution at high temperature have been found to recrystallise into small equiaxial grains on annealing at 200° C. Little change was found on annealing the finer grained deposits produced at room temperature; nor did deformation, followed by annealing at 200° induce definite grain growth or recrystallisation. This suggests the presence of foreign matter in the deposit.

After annealing soft copper deposits (formed in an acid copper sulphate solution) at 900° C. for four hours in vacuo, the microstructure showed very large grains with little evidence of non-metallic matter. Hard, fine grained copper deposits (formed in a cyanide solution) recrystallised into very small equiaxial grains and a quantity of non-metallic matter was visible in the grain boundaries.

It thus appears probable that, as with nickel, the structure of copper and tin deposits (prepared as described) is refined by the inclusion of non-metallic matter during deposition.

2. Low Temperature Treatment.

Further extension of the technique of the effect of annealing is desirable in order to obtain more insight into the effect of basic matter, and also to

⁷ G. E. Gardam and D. J. Macnaughtan, *Trans. Faraday Soc.*, 1933, **29**, 755.

* Plate XLIII.

throw more light on the effect of hydrogen and its relation to stress in the deposit.

The most obvious mechanism whereby stress can be explained in terms of hydrogen is the volume change which occurs when hydrogen enters or leaves the metal. Thus, it is well known that nickel expands when subjected to the action of cathodically evolved hydrogen, returning to its previous volume when the treatment ceases. Taking this view, the stress would depend on the ratio of hydrogen to nickel discharged at the cathode. Stress measurements made by the authors confirm that such a general relationship holds. Further light on this question may be thrown by a study of the effect of low temperature heat-treatment. Preliminary results, for example, have indicated that relatively soft deposits, produced at low cathode efficiency, are highly stressed, and that the stress tends to increase on annealing at low temperatures (for example 200° C.). Harder deposits, produced at relatively high efficiency have only been found to be moderately stressed and though stress tends to be relieved on annealing at 200° C., little effect on hardness and no effect on microstructure was noticed as a result of this annealing treatment. These results are in line with those of Guichard and his co-workers, who found that all of the hydrogen could be removed from electrodeposited nickel and iron by low temperature annealing before any appreciable change in hardness was found; they support the suggestion that volume changes in nickel deposits are associated with hydrogen. The anomaly of relief of stress on low temperature annealing the hard deposits may be associated with the formation or extension of minute cracks; or it may be that the recrystallisation temperature of the very fine grained hard deposits is lower than that of the softer deposits, and that relief of stress therefore takes place at a lower temperature.

It is probable that hydrogen is not the only factor contributing to stress in nickel deposits. Thus, addition of colloids to the solution frequently causes an increase in the stress in the deposits, and the fact that hard nickel deposits, the hardness of which has been attributed to the effect of colloidal nickel compounds, do not always give an indication of high stress may be due to the marked tendency for cracks to be present in very hard nickel deposits. As previously mentioned, this emphasises the need for caution in the interpretation of stress results without reference to other methods of examination.

Summary and Conclusions.

The desirability of using metallurgical methods to throw light upon the structure of electrodeposited metals has been shown, and the importance of supplementing micro-examination by reliable physical tests of the deposit, both as produced and after heat-treatment, has been emphasised. Examination of the microstructure provides invaluable evidence which cannot be deduced with reliability from the surface appearance of the deposit; alone, however, it is inadequate, particularly with fine grained deposits in which substantial changes in structure (revealed by physical tests) are possible without appreciable changes in microstructure. A form of indentation hardness test, such as the Brinell or diamond pyramid test, can afford reliable, reproducible and comparable quantitative data to supplement the general indication given by the microscope and may be supplemented for special purposes by other physical tests, such as the tensile test. The combination of these methods in a study of nickel deposits, as formed, and also after heat-treatment, has shown their value and has demonstrated that colloidal nickel compounds (the presence of which was only revealed by heat-treatment) are important in determining grain size and physical properties. The use of low-temperature heat-treatment also gives promise of enabling a correlation to be made between stress and the amount of co-deposited hydrogen.

The application of these methods of study to deposits of other metals, such as tin, copper, iron, cobalt and chromium, appears likely to yield important results, and it appears possible that solid matter of a colloidal nature, such as hydroxide or basic salt, may be the cause of the small grain size of electrodeposited metals other than nickel. Chromium deposits have been shown to contain oxide both by analysis, by dissolution of the metal after heat-treatment, and by heat-treatment and micro-examination.

It remains to be established whether the high hardness of chromium is primarily due to oxide, and to what extent hydrogen may also contribute.

CHEMICAL AND PHYSICAL PROPERTIES OF ELECTROLYTICALLY DEPOSITED METALS IN RELATION TO THEIR STRUCTURE.

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It is generally accepted that metals produced by electrolytic refining are extremely pure. Nevertheless it has been known for a long time that impurities contained in the anode are still found—although in a smaller concentration—in the refined cathodic product. The following data relating to the electrolytic purification of iron can be quoted as an example :

TABLE I.

	C.	P.	Si.	S.	Mn.	Fe.
Anode, of Swedish iron .	0.260	0.007	0.109	0.007	0.021	99.596
Cathode, after a single refining	0.019	0.013	0.002	0.006	0	99.960

We must thus bear in mind that electrolytic metals are never *absolutely* pure. Without going into further details here, we must specially mention one well-known impurity, viz. hydrogen, occurring in electrolytic deposits, because it may seriously affect their properties. Hydrogen is often retained in considerable quantities by the metals deposited on the cathode. The following concentrations of hydrogen have been found by different observers :

TABLE II.

Metal.	H ₂ , Vol. %
Nickel, by Hessenbruch	79
" Guichard, Hausmann, Billon and Lanthony, up to	660
Tin	5-12
Iron, by Hughes	180
" Guichard, Hausmann, Billon and Lanthony	780-6000
Zinc, by v. Schwarz	2000
" Schlötter and Burmeister	82-820
Chromium, by Guichard and others	260000

Is the hydrogen "mechanically" retained by the deposit, or does it form an alloy with the metal? This question has been discussed by many investigators; we think that both kinds of occlusion occur simultaneously.* In a section of a nickel deposit the black points correspond to bubbles of mechanically occluded hydrogen. The fact that chemical binding occurs together with looser occlusion is proved by the fact that increasing amounts of hydrogen are liberated by heating up to 400° C. Between this temperature and 800° C. the amount of gas liberated increases very slowly; above 800° C. the curve rises again rapidly. The obvious interpretation is that up to 400° C. mechanically occluded hydrogen is liberated, and that the chemically bound hydrogen is released at much higher temperatures, above 800° C.

The mechanical occlusion of hydrogen by metals can be illustrated by using a strip of electrolytic nickel as cathode in an acid solution. On submitting this strip to a mechanical strain—for instance by bending it—we observe a liberation of gas in the form of bubbles. Another experiment showing the absorption of hydrogen by the cathode consists in fixing a foil of electrolytic nickel in front of a capillary and using it as a cathode. At first no gas appears in the capillary; but after a certain time the foil becomes saturated with hydrogen and the gas begins to diffuse into the capillary. The pressure under which the hydrogen is evolved can be measured by observing the displacement of the mercury thread in the capillary.

The amounts of hydrogen dissolved by a given metal vary very considerably. It would be interesting to know what conditions determine the amount of gas occluded. The investigations of my collaborators have given a definite solution to this problem:

1. At a given concentration of H-ions, the hydrogen content in the metal becomes smaller with rising current density.
2. At a given current density, the hydrogen content of the metal increases with rising acidity of the solution.

Various observations led us to the conviction that the properties of the electrolytic deposits depend not only on the conditions at the cathode but also on the kind of anions present in the solution.

In 1928 I formulated the rule that the structure of electrolytically produced metals is strongly influenced by the kind of salt used as electrolyte. The spatial arrangement in the molecules of the metallic salt is the factor which determines the appearance and structure of the crystalline deposit obtained on electrolysis. Billiter disputed the proof of this rule and particularly its general applicability, on the ground that it is not based on satisfactory experimental evidence. He overlooked the fact that, as Müller and Barchmann¹ have stated, the overvoltages observed during the cathodic deposition and the anodic dissolution of cadmium and zinc (in solutions of their simple salts) are actually dependent on the nature of the salt used. The curves showing the current density as a function of the cathodic and the anodic voltage are steepest for chlorides, and become gradually less steep with bromides, sulphates and perchlorates. The same authors found that the cadmium deposit obtained from a chloride solution is roughly crystalline, whereas the deposit obtained from sulphate has no visible crystalline structure. The authors thus established a connection

* Here Professor Schlotter showed a number of micro-photographs.

¹ *Z. Elektrochemie*, 1933.

between the size of the crystallites and the overvoltage, and found both to be dependent on the nature of the anions. *A higher voltage corresponds to a larger anion.* The same cause is effective in the absorption of hydrogen by metallic deposits; a higher overvoltage (due to a larger anion) is connected with a higher concentration of hydrogen in the metal. We have been able to prove this, for instance, in the case of zinc. The metal obtained from sulphate contains no more than 40 c.c. H₂ per gram atom, whereas the metal deposited from a solution of cresyl-sulphonic salt shows a hydrogen content of 77 c.c. per gram atom.

To illustrate the connection between the appearance of the crystals and the kind of the anion, we may compare the appearance of tin deposits obtained from stannous chloride, from sulphate, and from the phenol-sulphonic salt. The first two are roughly crystalline, whereas in the last no crystalline surfaces can be detected visually. We have later observed many interesting connections of this kind between the nature of metallic salt and the appearance of the deposit.

In studying the deposition of copper and silver from their iodides we have observed that under certain conditions appreciable quantities of iodine are found in the cathodic deposits. One could imagine a purely mechanical occlusion of complex metal iodide anions, enclosed between the crystallites of the metallic deposit. We have found, moreover, that when dealing with a solution of copper iodide, there occurs in the copper deposit a phase richer in copper iodide. The total amount of iodine found in copper depends on the current density (Table III).

TABLE III.

Current Density, amps./dm. ²	Iodine per gram of Deposit.
0.25	0.05 × 10 ⁻³ g.
0.50	0.15 " "
0.80	0.58 " "
1.00	1.27 " "

The determination of the crystal-lattice constant of this "iodised" copper reveals an expansion of the regular copper lattice; this expansion increases with rise in the iodine content of the copper deposit, at first slowly, later more quickly.

TABLE IV.

	Current Density, amps./dm. ²	Iodine per gram of Metal.	Atomic % of I.	Lattice Constant a in Å.
—	—	0.0	0.0	3.6042 ± 0.0002
1	0.25	< 0.05 × 10 ⁻³	< 0.025	3.6046 ± 0.0002
2	0.50	0.15 "	0.075	3.6049 ± 0.0002
3	0.80	0.58 "	0.29	3.6059 ± 0.0002
4	1.00	1.72 "	0.63	3.6094 ± 0.001

With silver, analogous results are obtained. X-ray photographs taken with the purest metal obtainable gave, in accordance with the data of Sachs and Weerts, a value 4.0775 ± 0.0002 Å. for the lattice constant, whereas silver deposited galvanically from the solution of its iodide (with current densities up to 20 amps/dm.²) and containing 0.99 per cent. of iodine (corresponding to 1.83 per cent. of AgI) has a constant equal to 4.0839 ± 0.0001 Å.

Our experiments have thus established two important new facts :

- (1) The anions can take part in the cathodic deposition ;
- (2) The anions* can enter the crystal lattices of the metals, changing the lattice constant.

The importance of the changes in the structure of the metals "contaminated" with anions* is clearly shown by the properties of iodised copper and silver. With silver, the most obvious effect is the change in the appearance of the deposit: instead of the usual white, it has a golden yellow colour, not to be distinguished from that of gold deposits. The gold-coloured nuclei which were formed on the edges of the cathode were extremely hard and could easily be pulverised. Under a microscope (magnification 500) no crystalline structure could be observed after etching with nitric acid. This was not unexpected, since the deposit had a lustre—thus showing that the single grains were of a size inferior to the wave-length of visible light.

Silver deposits containing less iodine have a white or yellowish colour; but they all have this remarkable property, that they do not blacken at all—or at most very little—when treated with hydrogen sulphide solution. Silver has thus lost its capacity for reacting with compounds of sulphur—and this to such a high degree that it is remarkable that the silver plating industry should have neglected the use of solutions of this kind for the production of silver coatings.

Equally interesting changes are observed with "iodised" copper. If a plate of iodine-containing copper exposed to sunlight so that one part is illuminated, the illuminated surface becomes blue, the non-illuminated remains red. This experiment is well reproducible.

Having observed the entering of anions* into the cathodic deposits of copper and silver we tried to get the same results with nickel, and we were successful in different ways. The following interesting changes were observed with nickel: When nickel oxide (or, more probably, hydroxide) is caused to enter the nickel lattice, a product is obtained which shows a high lustre and dissolves in a mixture of chromic and sulphuric acid leaving a black "skeleton." Parallel experiments with ordinary nickel deposits, however, showed that these are passive and can remain for days in such a mixture without dissolving. The "soluble" nickel has a different electric resistance; it forms a thermocouple with normal nickel, producing an E.M.F. equal to 2.5×10^{-6} volts per degree centigrade. For comparison, it may be mentioned that the E.M.F. of the thermocouple platinum/rhodium-platinum-alloy, 6×10^{-6} volts per degree. If a plate of oxide-containing nickel is caused to glow in a current of oxygen, there remains, after complete oxidation, a transparent, homogeneous, dark green foil; no patches of black oxide can be discovered in this foil under a microscope.

It has been known for twenty-five years that electrolytic iron has especially valuable qualities in respect to permeability, coercive force and magnetic remanescence. From the method of its production one may surmise that these properties are due to some characteristic arrangement of impurities contained in the crystal lattice of the metal.

The lustre, colour and hardness of chromium platings are not properties of the metal chromium, but must be traced back to chromium oxides contained in the metal lattice. If chromium is deposited from the solution of its chloride (using chromium anodes) the cathodic

metal is still lustrous, but resembles more a deposit of brilliant nickel. The typical bluish tone of a chromium deposit has vanished.

Our experiments have thus proved that the chemical and physical properties of electrolytically produced metals (we will be cautious and speak of them alone) are changed by allowing anions* to enter the crystal lattice. Different anions can be used—halogenides, oxides and hydroxides, sulphides (as in black nickel and black chromium), etc. A case of halogens entering a metal lattice is known from the work of Coehn on electrolytic antimony. But there, probably, oxy-halogenides are involved which are responsible for the explosive properties of the antimony so obtained. Explosive antimony can also be prepared from solutions of perchlorate.

X-ray photographs seem to prove that "iodised" silver has a tetragonal space-centred lattice; but we prefer not to consider this result as definitive. The X-ray diagrams are in places so complicated that specialists whom we asked for advice were unable to give a definite answer.

The conditions are still more complicated by the fact, confirmed by our experiments, that in addition to the anions* the metal still contains more or less of hydrogen. With nickel, the concentration of hydrogen is diminished by the oxide; but with tin it seems, on the contrary, to increase when we pass from the ordinary oxide-free metal to the electrolytic metal containing oxide.

In the case of steel, it is well known that the formation of different intermediary layers (ξ , δ , η , ζ) can give to hardened or tempered steel the most variable mechanic, magnetic, chemical and physical properties. The same thing can now be said about other metals. A collaboration of many scientists would be necessary to elucidate these complicated phenomena.

* German. *Anionartige Körper*.

ON "SOMATOID" ELEMENTS OF STRUCTURE IN ELECTROLYTIC METAL DEPOSITS.

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1.

By the term "somatoids" we mean small independent particles—mostly of crystalline structure—which possess a characteristic shape, but are nevertheless essentially different from true, perfect or only partially developed crystals. Unlike the lattice-structure of crystals, the internal structure of somatoids, although organised in an orderly fashion, is not homogeneous; the material is distributed in them in a characteristic fashion, and their outward appearance is determined by this distribution.

The formation of small bodies with typical internal and outward structure of this kind has been observed in a great number of different cases. As with the formation of crystals, it is not due to chance: a given substance appears, under identical conditions, always in the same

somatoid formations. But the somatoid form is not essentially a property of the material of which the somatoids consist: the same form can often be obtained with a great number of different substances.

The somatoids are to be considered as a distinct kind of "organised" matter. As such, they deserve our special interest and study, and must not be dismissed as "disturbed crystals."

2.

The investigation of the forms in which certain simple substances are precipitated under different conditions has, in the first place, shown the necessity of treating the somatoids as a distinct type of organised matter. This conception has since proved to be useful in the study of the morphological and chemical properties of many substances. It is beginning to be widely used in describing the systems called by Wo. Ostwald "systems with coarse discontinuity."

So far, the investigations of somatoids, carried out on many different objects,¹ have been chiefly concerned with the formation, properties and behaviour of single individual somatoids. On the other hand, it has already been stated that somatoids may form characteristic aggregations and are sometimes used as building-stones in the formation of larger two- or three-dimensional bodies. Amongst the former, electrolytic deposits of metals have been specially mentioned.

Wesselowski and Wassiliew² have recently discussed a rational system of disperse structures, and used it to describe the different kinds of graphite (all of which are chemically the same substance—carbon). The descriptions by these authors of the single species are based on the assumption of several orders of structural elements. The parameters and mutual relations of these elements determine the nature of a given disperse body. They distinguish the following orders:

1. *Crystallites* (as defined by Tammann) of all forms and sizes down to ultra-microns.
2. *Characteristic Aggregations of Crystallites* which play the rôle of bricks in the building-up of larger bodies (analogous to our "somatoids" or to the "micelles" of colloidal chemistry).
3. *Textures*, i.e. still larger elements, forming the greater part of macroscopic bodies.

This point of view appears to be useful in dealing with disperse structures, and can be further developed, especially when coupled with considerations arising from the *manner of growth* of the bodies. One of the fields where its application may be successful is that of *electrolytic metal-deposits*. The disperse nature of these deposits is evident, and the above classification can be used for describing their different types.

The "elements of the first order" in galvanic deposits are always crystallites. We propose now to call attention to somatoids as their "elements of the second order." This may be especially useful from the point of view of a rational classification of electrolytic deposits.

In certain cases the whole of an electrolytic deposit consists of somatoids. In other cases they appear only as single, albeit normal, constituents in a structure which, as a whole, is built up in a different

¹ *Helv. Chim. Acta*, 1925, 8, 451, 470, 697, 703; 1930, 13, 929; 1931, 14, 3, 305, 330, 1215; 1932, 15, 1425.

² *Z. Kristallographie*, 1934, 89A, 156.

fashion. Sometimes they play only a subordinate—often undesirable—rôle in the structure of electrolytic metals.

The following properties of electrolytic metal-deposits (the list is not a full one) are connected with the existence of somatoid elements : (1) The *rough structure* of deposits, depending on current-density and temperature ; (2) The occurrence of *excrescences* (including the majority of so-called " pits ") ; (3) The so-called " edge-spots " (*Randknospen*) ; (4) The characteristic *separation of the deposit into special regions or thickening* under the influence of colloidal or other additions to the electrolyte.

3.

In trying to understand the formation and the rôle played by somatoid elements in electrolytically deposited metals, we must make use of the results obtained previously in studying the elementary somatoids of chemical elements and simple compounds produced by reactions in solutions. We will therefore consider these results first.

We use now the notion of " somatoids " in its original sense—meaning small, but microscopically visible particles possessing a definite " organisation " acquired in the process of their formation. There exist forms intermediate between typical somatoids and larger aggregates of crystals ; it is therefore difficult to make a sharp rational delimitation on this side. At the other extreme, a continuous series of formations connects the somatoids with the " micelles " found in colloidal systems (as defined by Freundlich), which also may represent material elements in the building-up of matter, possessing definite structure and shape. This connection between somatoids and micelles permits some extrapolations to be made from the realm of microscopic somatoids to that of ultra-microscopic particles—especially since the conditions under which somatoids are formed sometimes resemble those under which colloid dispersions arise.

4.

The mere microscopic survey of somatoid elements as they occur in different natural materials or preparations does not reveal much of their nature. In the following description we shall therefore make use chiefly of investigations in which the physico-chemical conditions of the formation and the behaviour of the somatoids have been studied :

(a) As already mentioned above, the form and nature of somatoid formations do not in the first instance depend on the composition and crystallographic properties of the material involved : one and the same type of somatoid structure is often adopted by very different substances. Somatoids are morphological individuals characteristic of definite *states* realised during their formation rather than of definite *substances*.

(b) Somatoids may sometimes grow ; further material is added to an original formation. Nevertheless, there is no doubt that this characteristic formation itself can primarily arise only under the special conditions of the chemical reaction in which the substance of the somatoid has been formed.

(c) It is further found that somatoids of a given substance are probably never formed without the assistance of a second insoluble substance. This substance need not necessarily be a " foreign " one—*i.e.* a casual or intentional admixture ; this rôle may be played by unstable phases of the " principle " substances, or by products of reaction of the solvent

with these substances before or after the main process, or by other "normal" components of the reacting system.

(d) On the other hand, different substances "promoting" the formation of somatoids often give identical formations—thus indicating that their *state* and not their chemical composition is the essential point. In fact, *colloids* play the principle rôle; but the action of colloids depend upon their chemical nature as well as on their state of dispersion. Sometimes it appears possible to draw conclusions, from the form of somatoids, as to the nature and condition of "accessory" components which must have been present in the reacting system.

(e) The accessory components which have helped to form a certain type of somatoid, need not necessarily be found later in the somatoid formations. After having fulfilled their function, they may disappear in different ways. Most of the somatoids are therefore found to be practically homogeneous from the chemical point of view.

5.

The mechanism of the formation of somatoids must differ in different cases, and it is sometimes very complicated. Nevertheless certain general principles of formation can be propounded.

(a) A first and very important factor in the formation of somatoids is the combination of a chemical reaction with a "formation," process in the reaction zone. The inter-relation of these two renders precipitation an "organised" process, leading to the formation of a product possessing definite shape and structure.

(b) The somatoids are almost always products of a combined action of crystallisation forces with surface forces forming mobile masses. Both act simultaneously on two kinds of matter formed in the same space. Spherical drops and normal-shaped crystals are the two extremes between which a mean is sought and found.

The existence of some substance capable of producing definitely shaped (in the extreme case, spherical) formations under the influence of surface forces is one of the most important conditions in the production of somatoids. This condition must, for instance, account for the fact that all individual somatoids formed during a reaction possess very much the same size. Generally speaking, the rôle of surface forces lies in their faculty to sub-divide the whole reacting mass into small systems with a definite structure and characteristic dynamic properties. If the substance enclosed in one of these spaces undergoes chemical or morphological transformations a certain internal structure arises, changing also the outward shape of the small "reaction space" and fixing its contents. (Sometimes one observes, for instance, that crystal nuclei, formed inside colloidal drops or flocculates, develop within them like the embryo in an egg, changing the surrounding material or using it for their own growth, and adjusting their own shape in accordance with the space available in the drop. The confinement of the process to a limited space ensures its regularity and constancy of the end-product.

(c) The somatoids show peculiar properties also in their chemical behaviour. It is interesting, from this point of view, to observe that unstable forms of some substances may acquire a certain stability when produced as somatoids; their free energy must therefore be superior to that of the regular crystals of the same substance. Furthermore, it is noteworthy that higher chemical reactivity of somatoids is due not

only to their state of internal dispersion, but also to the fact that they sometimes possess something like special "reaction-organs" (that is to say, different parts of one and the same somatoid react in different ways). These properties are connected with the specific process of the continuous development of somatoids, as has already been mentioned.

6.

All these facts lead us to expect the *formation of somatoids in the electrolytic deposition of metals*. Galvanic deposition is, in fact, a crystallisation process strongly influenced by colloidal or other "secondary" components which may be present in the bath, as is well known from many practical examples. It is therefore permissible to consider electrolytic deposits from the aspect described above when dealing with individual somatoids of "chemical" origin, especially having regard to the fact that sometimes the characteristic features of electrolytic deposits clearly indicate their relation to somatoid systems. It is necessary, however, to bear in mind that the special conditions of the electrolytic processes are bound to modify to some extent the mechanism of the formation of somatoids.

(a) The most important factor is not the electric current in itself, but the fact that due to this current the precipitation must occur in *a definite place, viz.* on the surface of the cathode, as a consequence of which we have a typical *topochemical* reaction. The peculiar properties of such reactions have lately been studied by many investigators. One property is that, in a topochemical reaction involving the formation of a solid body, the chemical formation of the new product and its morphological development take place inside the same limited space. The connection between the process of formation and the body already formed is therefore closer than in reactions where they are not confined to a small space. The "localisation" of a topochemical reaction makes the chemical process especially well reproducible; on the other hand, this same condition adds importance to the possible influence of secondary factors—*e.g.*, small amounts of foreign substances.

(b) The locus of an electrolytic deposition is *the surface of the cathode, together with the adjoining layer of the electrolyte* (the so-called "cathodic film"). The discharge of ions of course occurs on the surface of the cathode itself; but closely connected with it are chemical reactions taking place in the "cathodic film" of the electrolyte—for instance, hydrolysis giving basic products and becoming especially noteworthy when the cathodic film grows weak in metal ions; desintegrations of complex anions containing metal salts, etc. These reactions produce colloidal substances of differing chemical nature and dispersion and bring about conditions under which the crystallisation of the metal is coupled with production of different "accessory" substances. These are the conditions which we know to be favourable for the formation of single somatoids. Owing to the topochemical character of the process, very small quantities of "accessory" substances formed in the cathodic film may serve to exert considerable influence on the structure of the deposit, especially if they are positive colloids and as such themselves attracted by the cathode.

(c) The effects actually observed depend on the special conditions of the electrolysis. They may be limited to the production of smooth fine-grained or highly-disperse metal layers, instead of coarse deposits,

as is well known in many practical cases. This change in the character of the metal surface is chiefly due to the colloid substance covering the cathode with a kind of thin network layer, thus causing the crystal nuclei to be uniformly distributed all over the surface and retarding their extensive growth. The characteristic features of this phenomenon have been described in the earlier work of the author³ and fully cleared up since in the recent excellent work of Macnaughtan.⁴ The "accessory" substances are in this case themselves more or less completely reduced in the course of reaction. The metal-deposit is thus built up from two different primary materials—from the ions of the solution and from the insoluble "accessory" substance.

(d) The processes on the cathode will generally proceed in this way so long as the amount of the reaction products in the cathodic layer remains small. If, under the special conditions of the electrolysis, this amount becomes larger, and the colloidal film which is "pressed" against the cathode grows thicker and changes its structure, new developments may occur, which depend upon the production of movable masses formed by surface forces. Here we enter into the region where the conditions are favourable for the development of somatoids: the sphere of reaction becomes divided into a great number of separate small spots. The electrochemical reduction starts in all of them and causes an internal crystallisation and ultimately a fixation of the reacting mass in a great number of small bodies.

7.

We cannot enter here into the details of the processes involved; to give an adequate description it would be necessary to discuss too many different experiments and problems. Not only may purely electrochemical influence the formation of the deposit but also the mechanical and the hydrodynamical conditions accompanying the electrolytic process on the cathode. We may mention for instance the rôle played by convection currents; or the influence, hitherto practically disregarded, which vortices may have in the formation of somatoids. The beautiful investigation of Hatschek⁵ has laid the foundation for the discussion of this latter effect.

We intend to give a full description of our experiments with the somatoids elsewhere. Our main purpose in this contribution is to draw the attention of electro-chemists to the fact that certain effects well known to them are in no way specific for the electrochemical process. Our experiments have had as their starting-point the above-mentioned undesirable effects observed in some galvanic processes. We have therefore worked with such metals and under such conditions as would lead to emphasis of these "secondary" effects—sometimes turning them into the main process on the cathode.

We have studied from this point of view, partly in connection with our earlier, preliminary work, the galvanic precipitation of a number of metals; we have often used in these experiments electrolytes which are not commonly in use in practical electrochemistry.

The result is, that the same characteristic properties which have been found with single isolated somatoids, are also shown by the structural ele-

³ *Z. Elektrochemie*, 1913, **13**, 172, 181.

⁴ *Trans. Faraday Soc.*, 1928, **24**, 497; 1930, **27**, 633; 1933, **29**, 729.

⁵ *Proc. Roy. Soc.*, 1919, **A95**, 303.

ments of the electrolytic deposits and can be explained from the conditions under which they are produced.

We quote a few examples: The case of a *complete metallic layer* composed of typical somatoid elements can be well realised with chromium and with so-called "acetate-copper." With these metals we also made observations on the *edge-spots* whereby we were able to characterise them as typical somatoid formations. The growth of somatoid *excrescences* on many metals can be caused by simple means and explained as due to well-defined influences. Using as an example the cathodic precipitation of copper from copper sulphate solution we found that the *rough texture* which the deposit shows at higher current-densities is due to the formation of small uniformly distributed "reaction-spots" on the cathode; inside these spots the metal deposit is enclosed in a colloidal medium, which surrounds it and influences its development. Ultra-microscopic observation of the process shows the development as of quite the same nature as is shown, for deposits already developed to a higher degree, by the beautiful section-photographs of Portevin and Cymboliste.*

8.

The study of somatoids may have a *practical* interest; the occurrence of such elements is often disturbing, and the best way to avoid undesirable effects is to explore their causes and prevent their occurrence. A more *general* significance of our experiments consists in the possibility they offer of gaining some knowledge of the *conditions prevailing in the cathodic film* by using *morphological methods*. The structure of the cathodic film is a most important question in all kinds of electrolytic processes, and our knowledge of it is, so far, very meagre indeed. The somatoid structure observed in a deposit gives evidence of the conditions existing on the surface of the cathode and in the cathodic film during the electrolysis. The somatoid formations in the metal reveal the discontinuities (of distribution of matter, or of the conditions of space, time or energy) which existed in the cathodic space and which otherwise it would be difficult to recognise. Even in the cases where no such discontinuities are revealed by some coarse somatoid deposit, we must reckon with the possibility of their existence. The more or less continuous series of phenomena leading from the coarse deposits of obviously somatoid character to the finer effects of colloidal substances on the properties of electrochemical deposits permit us to make extrapolations in this direction.

9.

Some idea of the nature of the objects with which we are dealing is given by Figs. 1 to 6.*

Figs. 1(a) and (b) show edge-spots and spherical somatoid structural elements in deposits from "acetate-copper"; it can be seen that formations of the same type appear both as "*edge-spots*" and also constitute the layer on the cathode *surface*.

Fig. 2(a) shows particularly well the excrescences (also deposited from "acetate-copper") which the aggregates of spherical somatoids form as a whole. The difference in appearance of the upper and the lower part

* *Rév. Métallurgie*, 1933, 30, 323.

* Plates XLIV and XLV.

is due to the fact that on the latter further metal has been deposited. Fig. 2(b) shows the interior of a particle laid out in sectors.

Figs. 3(a) and (b) are parts of a chromium deposit. In Fig. 3(a) the shell-like structure of the somatoid is apparent. Fig. 3(b) shows a particle in section; the different appearance of the metal within and without, due to its origin from different primary materials (ions from the solution and colloidal matter).

In Fig. 4 we see excrescences on a silver deposit obtained from an ammoniacal solution, which is brought about arbitrarily by the deposit of small masses of zinc ions with very small current densities (0.75 ma./cm.^2). These are not due to hydrogen bubbles.

Figs. 5 and 6. These are not examples of electrolytic products but are isolated somatoids brought about in solution by ionic precipitation. Fig. 5—copper oxalate—shows very clearly that the structure arises from the concurrence of surface forces and crystallisation phenomena bringing about the shaping of mobile masses. In Fig. 6—calcium carbonate—the compound consists of the unstable modification "vaterite"; the radiating inner structure is well shown under polarised light. This provides an example of the fact that unstable modifications can become stabilised if they appear as somatoids.

THE EFFECTS OF FILM FORMATION ON THE STRUCTURE OF ELECTRO-DEPOSITED METALLIC COATINGS.

BY E. LIEBREICH.

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When Faraday made his famous investigations on the electrolysis of aqueous solutions, he and his contemporaries did not fail to notice that complications will often arise, not only at the anode, but also—and perhaps more commonly—on the cathode. These purely chemical complications are caused by side-reactions, due to the new products formed on the electrodes and the changes which occur in the composition of the solution in the immediate neighbourhood of the cathode under the influence of the current. The more electrolysis was studied by pure physicists the less was attention paid to these side-reactions and thus, it became the custom to consider the behaviour of the cathode as of a purely physical nature.

Chemical reactions can arise in two ways: Firstly, the electrolyte may react with the metal of the cathode, even when no current is flowing, or, secondly—and this is the more important case—the p_H value of the solution may increase near the cathode owing to passage of current, thus producing complexes of a colloid character in the solution, which are cataphoretically conducted to the cathode. Moreover, the increased hydroxyl ion concentration can give rise to the formation, on the surface of the cathode, of basic salts or hydroxides of the metal. An increase of polarisation follows in consequence of an increased transfer resistance, together with a larger consumption of energy for cleaning the cathode (by chemical reduction or mechanical removal of the products by the hydrogen bubbles leaving the surface); in other words, the appearance of an overvoltage effect.

It is out of place, here, to investigate how far, if at all, the phenomenon of overvoltage may be explained chemically, but the extent to which these chemical changes influence the form of metallic deposits on the cathode will be discussed.

The fact that these chemical changes control the character of the metallic deposits was first shown by the school of Kohlschütter, which directed attention to the influence of the hydroxides formed in the solution in the neighbourhood of the cathode under the influence of the current.

Osterle¹ has stated that these hydroxides will act as dispersing media favouring the formation of nuclei and preventing the growth of crystals. It seems to be a fact that these hydroxides control the formation of bright and fine-grained deposits to a much greater extent than the stirring effect of hydrogen bubbles near the cathode, to which Professor Kohlschütter, in his earlier researches, attributed the prevailing formation of nuclei. Some contradictions between experimental results and theory can be explained thus. The views of Osterle regarding the possibility of reactions in the neighbourhood of the cathode are completely in accordance with the views of Wiederholt and myself, derived from optical investigations of the behaviour of wire cathodes using the *Schlierenmethode*. According to these results, there seems to be no doubt that even at the lowest current-densities, the conditions favourable to the formation of hydroxides start to exist at the boundary between solution and cathode.

Nevertheless, the work of Osterle does not go sufficiently far, since he considers the influence of the hydroxyl ions only on the solution itself, and not on the metal of the cathode. Osterle is quite right in saying that the hydroxides of nickel formed in his solutions migrate by cataphoresis to the cathode, acting there to decrease the grain size of the deposit. He shows that the deposit becomes more crystalline on increase of the acidity of the bath or increase of temperature, proving this by the magnetic susceptibility of his deposits. But he neglects the influence of the hydroxyl ions on the metal of the cathode itself. If he had regard to this circumstance, Osterle must give another explanation than that which he provided for the fact that deposits on metals of low hydrogen overvoltage are less crystalline than those on metals of higher overvoltage. Osterle believes that a larger proportion of hydroxides can be formed on metals with a lower over-voltage than on metals with high over-voltage, and that, therefore, the dispersing media are present in larger quantities in the case of metals with low over-voltage than in the case of higher over-voltage. I cannot agree with this explanation, since the number of the hydroxyl ions produced at the cathode depends only upon the number of the hydrogen ions discharged there, and the effect must be the same whether the liberated hydrogen leaves the cathode as bubbles, or disappears by absorption, or in any other way. That is to say, the number of the hydroxyl ions is independent of the over-voltage, and is given by the number of coulombs passing across the cathode surface.

On the other hand, the reactivity of the various metals which may be used as cathode is different, and the extent to which the cathode surface undergoes chemical change depends, therefore, on the particular metal employed. Let us take, for example, platinum and silver, the cathodic

¹ K. M. Osterle, *Zur Kenntnis der Vorgänge an der Kathode bei der elektrolytischen Nickel-Abscheidung*. Promotionsarbeit, Zürich, 1928.

metals cited by Osterle, and as electrolyte take a solution of nickel sulphate. Comparing the cathode potential/current density curves obtained, using wire cathodes, it is found that platinum shows a very

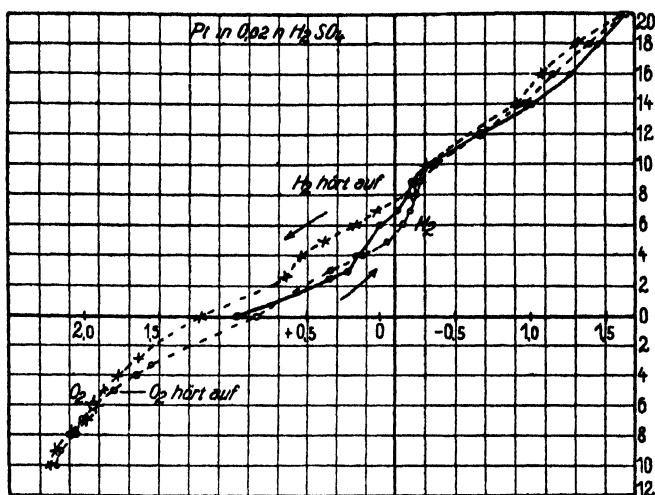


FIG. 1.

slight period of reaction in the critical parts of the curve, which lies always just below the visible evolution of hydrogen, whilst silver exhibits a very marked inflexion at this point. These inflexions and the arrest

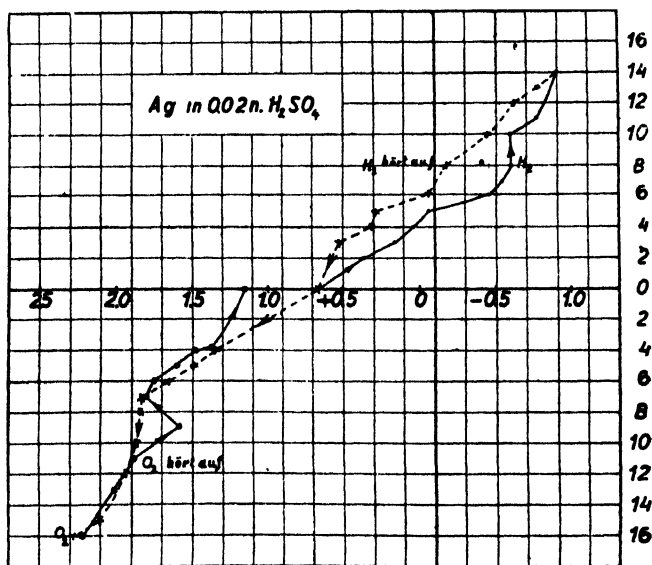


FIG. 2.

of potential thereafter may be explained as follows : Metals which show only a slight period of reaction may be covered with a very thin but homogeneous film, which therefore will not be removed by hydrogen and, if reduced, will speedily be reformed by the action of the hydroxyl

ions, the hydrogen being discharged uniformly. On the other hand, if metals show a very pronounced inflexion, and therefore a large tendency to react, this means that the film on the surface will be readily reduced by the hydrogen discharged and that, therefore, the metal will be in an active state. As the metal reacts in this state with the hydroxyl ions formed on the cathode, hydroxides or basic salts of the metal will be formed. Now, it depends on the solubility of these products whether a new film is formed or whether the surface of the metal remains in the active state. In the case where the solubility is small, a new film will be formed, the curve rising with increase of potential, and hydrogen being discharged at certain discrete points, where the film may just be destroyed in the other case the curve rising with decrease of potential, the hydrogen at a given current density being discharged to a much larger extent.

The behaviour of the silver curve shows that the surface of the metal remains in an active state, the basic sulphate of silver being sufficiently soluble. As soon, however, as chlorine ions replace the sulphate ions, the curve rises with increase of positive potential in consequence of the insolubility of the chloride of silver.

The explanation, therefore, for the difference in the nickel deposits on platinum and silver in solutions of nickel sulphate seems to be that on platinum the thin film of oxides may act as a dispersing medium, whilst on silver the surface of the electrode is uncovered, and therefore in an active state.

The conditions may not always be such that where oxides or hydroxides are formed the deposits will appear bright. This will depend on the proportion of the complexes formed relatively to the number of free metal ions, and also on the sign of the electric charge of the complexes and on other factors; and last, but not least, on the physical structure and behaviour of the films they form.

The conditions to be maintained for producing bright deposits, therefore, differ widely, and are very complicated. But this does not reflect the main principle that, in the absence of dispersing medium, bright deposits will not be obtained, and that hydroxides or oxides covering the surface of the cathode metal can act as dispersing media.

The rôle of the hydroxides formed by the current may, however, be more extensive, since in certain cases, the oxides formed in this way are essential for the production of metallic coatings on the cathode, which in such cases are still fine-grained, or bright. These cases are met when chromium is deposited from solutions of chromic acid. It will be worth while to examine this more closely.

The equilibrium-potential $\text{Cr} \rightarrow \text{Cr}^{++}$ is so highly negative that it would seem to be hopeless to attempt to deposit chromium from such a strongly acid solution, even on cathodes of high hydrogen over-voltage, in the absence of knowledge of the special characteristics of the behaviour of this acid. Surprisingly, however, a very high over-voltage is developed and it is found that this is due to a film of oxides of chromium formed by the current. The very high polarisation which develops on electrolysing chromic acid does not originate in any high transfer resistance on the cathode, but, as can be proved, is due to the consumption of energy necessary to reduce the film by hydrogen ions discharged on the cathode. It seems to me important to insist that, in this case, the over-voltage is not caused physically, *i.e.*, by electrical resistance, but by purely chemical effects, *viz.*, the reduction of a film produced by the current.

If ever the deposition of a metal is due to the existence of a film of

oxides, a careful examination of the details of chromium deposition will show how much the nature of the cathodic metal itself can affect the results.

Let us first take the case where we have, as cathode, a metal which does not react with chromic acid and is incapable of occluding gases, for example, gold. Now pass through the cell a very small current. Reduction will then take place on the cathode to a very small extent, indicating that trivalent oxides of chromium are formed, producing chromates of a colloid character in the chromic acid. These chromates, bearing a positive charge, migrate to the cathode and are attached to its surface. This film has no noticeable electrical resistance, but absorbs the hydrogen discharged on the cathode, and is therefore reduced to oxides of lower valency. The cathodic potential, therefore, becomes more and more negative, at first very slowly, later by sudden jumps, reaching finally potentials which correspond to the reduction potential of chromous ions to chromium metal. The quantities of chromous ions may be very small, and the yield of metal, therefore, is also very small. The metal, covered outside with hydroxides, but revealable by removing the film by acids, is quite bright. Here we have a very good proof that deposition in a dispersing medium gives rise to the formation of a large number of nuclei, but prevents any growth of metallic crystals. Changing now the cathodic metal, we see how far the conditions change. Let us take platinum. This metal is distinguished by its property of absorbing gases. Here we find, on using the same current, practically no trace of film formed on the cathode. It may be undecided whether this phenomenon is due to the solubility of hydrogen in platinum and the velocity of decomposition of platinum hydrides, or perhaps to its spongy structure, or, as Müller believes, to the high degree of resistance of oxides of platinum to reduction. In any case, it must be noted that by using platinum instead of gold, a film is formed only to a very small extent. As a result, the cathode potential becomes steady as soon as it reaches zero voltage, *i.e.*, at the equilibrium-potential of hydrogen, gas is evolved and the curve rises to higher current values when the potentials are such as to favour hydrogen development. The cathode then remains free from any metallic deposit. Only if the current density is extremely high does the curve bend, showing that now the film is starting to form and that conditions are suitable for the deposition of chromium metal. The formation and reduction of the film by these currents proceeds so quickly that the coating, instead of being bright and quite continuous, appears as a greyish and powdery deposit, slightly covered with a film of oxides (or with oxides included in the deposit). This greyish deposit may also be obtained on cathodes of gold, if we choose the same current densities, but with this difference, that under less extreme conditions chromium will appear on gold and not on platinum, thus proving the influence of the underlying cathode metal on the formation of the deposits.

Let us now, however, take cathodes of less noble metals.

We meet here a phenomenon which is very surprising. All metals, except platinum and gold, dissolve when cathodically polarised, if the conditions are not such as to lead to evolution of hydrogen. This phenomenon is the more surprising in the case of iron which is known to be passive in chromic acid solutions. It may be explained by considering that, as a result of cathodic reduction, the chromic acid on the cathode loses its oxidising character and acts only as pure acid. But this explanation is not exhaustive. Studying the same phenomenon with cathodes of

copper, which react with chromic acid even without any polarisation, it can be proved that copper dissolves to a much greater degree if cathodically polarised so long as hydrogen is not evolved. We see, therefore, that metals may react even when cathodically polarised, and we find the same phenomenon, but to a much larger extent (as Wiederholt and I recognised) in the case of all metals in dilute sulphuric acid. The explanation I offer for this is as follows, referring especially to my careful investigations made with cathodes of zinc in sulphuric acid.² The hydrogen ions, as they commence to be discharged under the influence of weak polarising forces, tend to reduce the films covering the metals which were formed by previous contact with the atmosphere. In consequence, the surface of the metal will be more or less bare, showing very active (*i.e.*, negative) potentials. This is what we call the reaction period in the curve. Only if by increasing the current, more hydrogen ions are discharged and an excess of hydroxyl ions exists in the neighbourhood of the cathode, will the latter react with the metal and form either hydroxides or, in combination with the anions of the solution, basic salts, which make it possible to cover the surface of the cathode.

In the case of chromic acid, the formation of chromates of the metals will be observed, and these are soluble in the chromic acid, and accompany the chromi-chromates formed by reduction of the solution. In this way the film will become thicker, and change in colour from golden to dark brown or yellow-brown in accordance with the different chromates present. It seems, however, that the physical properties, also, are changed, thereby varying the conditions for the formation of nuclei, since on copper a very bright deposit will be found, but on iron a somewhat greyish, and on zinc and other metals a very grey deposit. It can be seen that the form of the deposit really depends on the physical properties of the film; that is to say, whether the film is gelatinous or amorphous is ascertained by adding small quantities of acids and seeing whether basic salts are formed. The special influence of basic salts on the deposition of the metal can be explained only by the influence of the different salts on the physical and chemical properties of the film. It appears, indeed, that the colour and the physical structure of the non-metallic deposit changes from acid to acid. Thus it is found that on adding sulphuric or hydrofluoric acid, and using currents of 0.5 amp./cm.², a splendid bright deposit is produced, but, by adding fluosilicic acid (independent of the current density) the deposit has a rough surface, typical for this acid; again, by addition of chloric acid a grey deposit forms with other acids, such as hydrobromic or bromic, it is somewhat difficult to get deposits at all, and the metal has a poor and stained appearance. In the case of hydriodic acid, there is no deposit. It is important that by a certain degree of solubility, the film should form and dissolve continually, maintaining a certain and definite thickness. This follows from the fact that in cases where, at ordinary temperatures, greyish deposits are obtained, bright deposits are obtained at higher temperatures (30° or 40° C.). But this form of deposit, again, is confined to certain limits of current density. We can thus see, by taking as example, chromium, which never deposits in a crystalline but always in an amorphous form, and which, as we know, is always deposited in dispersing-media, that, in fact, the electrolysed solution can itself produce the dispersing medium necessary for producing amorphous deposits on the cathode. The conditions, however, which are suitable for the pro-

² *Z. physikal. Chem.*, 156A, 51, 1931.

duction of its desired bright deposits are, for the most part somewhat delicate, and are so little explored (I mention only the changing of the sense of migration of the complexes as a function of the acidity) that actually there is no other help than that of empiricism. Nevertheless, there is all the more a rich domain of research for scientific workers.

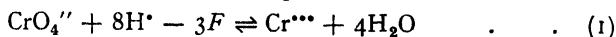
THE CATHODIC FILM IN THE ELECTROLYTIC REDUCTION OF AQUEOUS CHROMIC ACID SOLUTIONS.¹

BY ERICH MÜLLER.

Received in German, 28th January, 1935, and translated by E. W. Parker.

It is a surprising phenomenon ² that aqueous solutions of very pure chromic acid, in spite of their inherent strongly oxidising properties, remain practically unreduced on passage of current when smooth platinum cathodes are used. As in the case of solutions of passive sulphuric acid, evolution of gaseous hydrogen is the only effect of the electrolysis. This peculiarity in behaviour has been attributed to the fact that although reduction of chromic acid actually takes place, it is immediately interrupted by the formation of a difficultly soluble compound, chromium chromate, which builds itself up on the cathode in ordered molecules as an adherent porous wall, diaphragm ³ or film (Fig. 9). The chromic acid is then unable to penetrate into the pores of the film, *i.e.*, it can no longer reach the cathode, and therefore ceases to be reduced. The film is pervious to the small hydrogen ion.

If, however, even small amounts of foreign anions, *e.g.*, HSO_4' , are present in the solution, the chromic acid is reduced at the platinum cathode. The difference in behaviour in the presence or absence of SO_4 can best be demonstrated by the form of the cathodic potential curve shown in Fig. 1. Let a be the reversible potential of the reaction



and c the hydrogen potential. $a-c-r$ is the course of the current potential curve in very pure chromic acid (no current passes until the H-potential is reached and evolution of gaseous hydrogen takes place), and $a-b-n$ the curve obtained in solutions containing SO_4 (flow of current *prior* to attaining the H-potential, accompanied by reduction of Cr(6) to Cr(3).

If the absence of the reduction in very pure chromic acid is due to the *existence* of the diaphragm, the reduction occurring in the presence of SO_4 must be attributable to its *removal* or *dissolution*. If, however, the dissolution were unconditional in the presence of SO_4 , the presence of this constituent would necessarily give rise to a curve of the form shown in the dotted line ($a-m$), such as would be expected if reaction (1) proceeded without any interruption. This, however, is not the case. The reduction does not occur at potential a , but only at the much higher

¹ The greater part of the experimental work reported in this paper was carried out by Donald W. Light (*Dissertation*; Dresden, 1934).

² *Z. Elektrochemie*, 1926, **32**, 399; 1927, **33**, 72; 1929, **35**, 84, 222; 1930, **36**, 2; 1932, **38**, 205; 1934, **40**, 226.

³ First reports on the formation of this diaphragm see *Z. Elektrochemie*, 1899, **5**, 469; 1901, **7**, 398, 509; 1902, **8**, 231, 909; 1904, **10**, 49.

potential *b*. It is therefore obvious that only when a certain minimum voltage is present at the cathode can the SO_4 dissolve away the diaphragm.

These observations have been explained as follows: The HSO_4 is not capable, of itself, of dissolving away the diaphragm, but can accomplish the reaction only if it is drawn, with the H^+ ions, into the pores of the diaphragm by means of electrostatic forces (Fig. 9a). The chromic acid is not drawn in because its anion is too large (Fig. 9b).

It is further a very remarkable fact that, at carbon cathodes, reduction of very pure chromic acid takes place up to quite considerable current densities, even in the absence of foreign anions. Up to the present, the cause of this discrepancy in behaviour between smooth platinum cathodes and carbon cathodes has only been guessed at. A closer study of the reactions occurring at carbon cathodes gave promise of yielding further information on this point, and on the mechanism of the formation of the diaphragm and the nature of the film.

Current density-potential curves were first taken in the usual way. The voltage between the carbon cathode and a platinum anode was raised by small steps, and, three minutes after each increase of voltage, readings were taken of current density and of potential against a normal

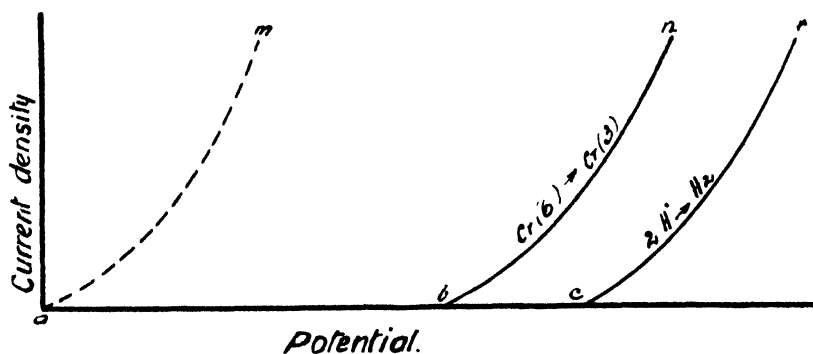


FIG. 1.

calomel electrode. Readings were taken in very pure chromic acid and in chromic acid solutions containing varying amounts of K_2SO_4 .⁴ In both cases the chromic acid was 30 per cent. strength. Temperature was kept constant at 30° by means of a thermostat.

The carbon cathodes were in the form of small rods of different makes, turned to a cross-section of 2 mm.² They were insulated with paraffin except on the end, so that the current impinged only on this portion, which had been carefully polished. The rods were inserted into the electrolysing vessel from below; their non-insulated surface lay horizontal, and about 5 cm. above them, also in a horizontal position, was placed a sheet of platinum, 10 cm.² The syphon leading to the normal calomel electrode ended 1 mm. below and close to the carbon surface.

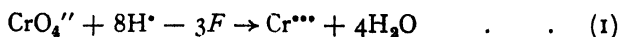
For certain sections of the curves which appeared especially interesting, oscillographic records were made of periodic changes in current density and potential occurring under conditions of constant voltage. A large amount of experimental data was accumulated, of which only sufficient is reported below to illustrate certain important points.

Fig. 2 shows a cathodic potential curve at a carbon cathode, in very pure chromic acid solution. With increasing voltage the current density

⁴ K_2SO_4 was added rather than H_2SO_4 , in order to keep the H^+ ion concentration as constant as possible.

risers steadily from the zero potential *a* (the potential of the carbon in the chromic acid without passage of current) up to a small "hump" at *m*, and after reaching a maximum at *b* again falls. Up to *n* a certain value can be read off for the current density and potential corresponding to each voltage; the values alter by only small amounts and the curve runs smoothly in one direction. Immediately an attempt is made to raise the voltage above *n*, however, the values for current density and potential jump to *v*. It is impossible to fix any values between *n* and *v*. At voltages above *v* the steady course of the curve is resumed. Over the whole range *a-b-n-c-d* the reaction at the cathode consists in a transformation of Cr(6) to Cr(3). Above *d* gaseous hydrogen is formed.

Concentration polarisation occurs on the section *a-b*. With rising current density, the extent of the reaction



increases. The solution at the cathode becomes progressively im-

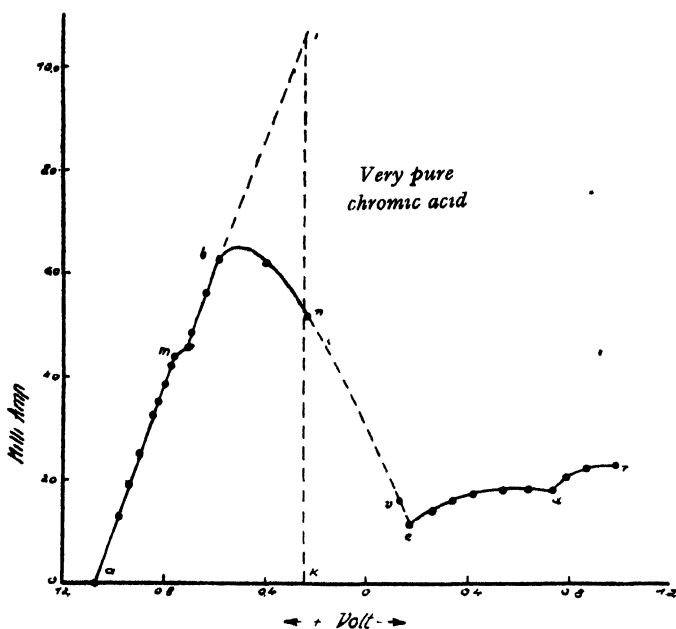


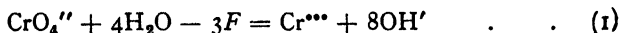
FIG. 2.

poverished in H^+ ion, until finally the formation of the difficultly soluble chromium chromate becomes possible, and formation of the film commences. The fact that the "jump" does not occur immediately on reaching the maximum at *b* (but only at *n*) indicates that the potential or voltage requisite for the formation of the film is not simultaneously reached over the whole surface of the electrode.

Starting from *b*, filming of the electrode proceeds only in proportion as the voltage is raised, whereas from *n* onwards, the portion of the surface still remaining bare is instantaneously covered, with the exception of a small residual area. This indicates that different current densities are present at different parts of the cathode surface. I assume that a large number of points of varying size jut out from the plane surface into the solution. The film first forms at these points, which are the regions at which the highest current density is operative, and subsequently spreads, as the voltage is raised, towards the plane surface. When the flat surface is reached there is a sudden and instantaneous

spread of the film over the whole of the plane surface ($n-v$). A perpendicular dropped through n on to the axis of the abscissæ cuts the extension of $a-b$ at i ; i would thus be the current density which would be observed at this voltage if the cathode remained unfilmed (bare), and $i:n : n-k$ would be the ratio of the even to the uneven surface of the carbon cathode.

The peculiar course of the potential curves provides a possible explanation for the divergence in behaviour observed between smooth cathodes of platinum and carbon cathodes. On a perfectly smooth electrode the reaction



will begin simultaneously at all the molecules on the surface, due to the presence on all sides of equal current density. The OH' ions formed will

find no chromic acid available for neutralisation, and will therefore cause precipitation of chromic chromate before they can be neutralised by an excess of chromic acid. If, however, the formation of the chromic chromate once takes place over the plane surface, the ordered character of the molecules and their

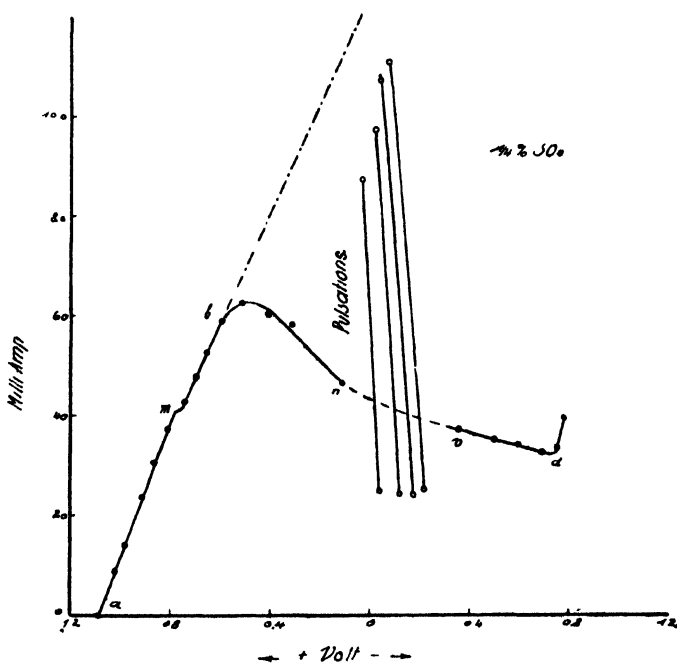


FIG. 3.

dense packing prevent access to the basic constituent of these molecules, of the chromic acid required for the dissolution.

Conditions, however, are otherwise, if the potential required for the reduction of the chromic acid is reached only at a point, where, side by side, the unchanged molecules are present and can neutralise the OH' ions before these can react to cause formation of the solid chromic chromate.

If, therefore, with rising voltage, the film has progressed as far as the base of the points ($b-n$), a further increase in voltage will result in a sudden filming of the whole plane surface ($n-v$). The fact that reaction (1) still takes place over a small range ($c-d$) may be explained as follows:—

Behind the film a charge of electrons is dammed up. On plane surfaces the chromic acid cannot be drawn into the pores by electrostatic means (Fig. 9b) because it is too large, but it enters at the points (at which obviously the diaphragm must be split open (Fig. 9c), with resulting destruction of the film. It should also be noted that curves of the type shown in Fig. 2 are not exactly reproducible. Their form is, broadly speaking, similar, but the maximum b , the potential at which the "jump" occurs (n), and the horizontal section ($c-d$) vary in height, their position being contingent on the nature of the carbon and its surface condition, as would be anticipated from the foregoing observations.

Fig. 3 is the potential curve obtained in the presence of 0.25 per cent. of K_2SO_4 ; Fig. 4, the curve with 2 per cent. K_2SO_4 . Curves of the form of Fig. 3 occur with low sulphate contents (less than 1 per cent.), while the type shown in Fig. 4 is characteristic for solutions containing over 1 per cent. It is found that the form of the curve from a to n is always

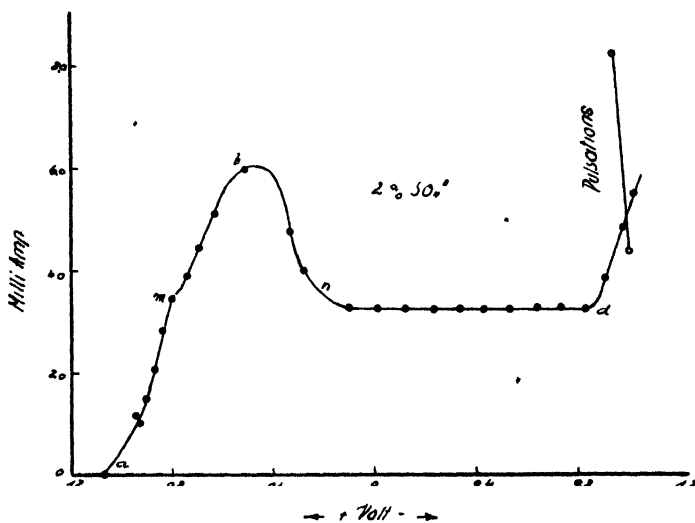


FIG. 4.

similar in very pure chromic acid, whether SO_4 is present or not; no difference occurs until the voltage is above that of the "jump" value. This fact clearly confirms the conclusions drawn from the experiments with smooth platinum cathodes, *viz.*, that the effect of the foreign anions becomes operative only after a certain minimum potential is reached, namely, the "draw-in" potential (*Einbezugspotential*), which must lie above that at which the "jump" occurs.

In solutions of low sulphate content (Fig. 3), after the "jump" potential has been reached, characteristic pulsations of current density and potential are observed; the range of these fluctuations widens with increasing voltage. Fig. 5*, a section of an oscillogram, is typical of these effects. This relates to a fixed and constant voltage only. Oscillograms of this type were taken with various voltages, and different concentrations of SO_4 , within the range subject to the pulsation effect ($n-v$) (Fig. 3). Lack of space precludes reproduction of the whole series. For the present purpose, moreover, interest centres rather on the *form* of the periodic

fluctuations, which remains substantially similar, except that the periods becomes shorter as the SO_4 content is increased (Fig. 5 *). To illustrate these points, the highest and lowest values of current density and corresponding potential for a periodic phase are shown (as circles) in Fig. 3; the values relating to any given voltage are joined by a straight line. These lines cut the dotted connecting line (nv , Fig. 3) at points which may be regarded as the current densities and potentials which would be observed if the fluctuations did not occur.

It should be noted that the highest limiting value for current density (Fig. 3) extends close up to the extension of the line $a-b$, which represents the current densities which would be observed if no diaphragm were present at the respective voltages, indicating that the highest value corresponds to a condition in which the electrode is momentarily bare (unfilmed). The lower limiting values, on the other hand, lie at various points below the potential (n) at which the "jump" takes place in very pure chromic acid solutions, but not so low as the minimum value observed with that solution (Fig. 2, $c-d$). This indicates that during the fluctuations, a condition of *almost* complete filming is attained.

If the voltage is raised beyond a certain value, the periodic pulsations cease. A horizontal section ($v-d$) ensues on the curve, and no further rise in current occurs until the potential is reached which corresponds to the evolution of hydrogen (d , Fig. 3).

With high sulphate (more than 1.2 per cent.) these fluctuations no longer occur (Fig. 4). After the bend beyond the peak on the curve there follows immediately a horizontal section (nd); the higher the SO_4 concentration, the higher, apparently, is the position of this portion of the curve. When evolution of hydrogen begins, the curve again takes an upward bend. With high concentration of SO_4 a new type of fluctuation occurs at this stage, a typical example is shown in Fig. 6.*

The limits of current density and corresponding potential for a single voltage are shown as circles in Fig. 4, and are joined by a straight line. After a given voltage is passed, these fluctuations also cease.

An attempt will now be made to explain these phenomena. For the sake of simplicity, we will imagine that cones of equal size, ending in sharp points, have grown out from the plane carbon surface; a typical excrescence is shown in Fig. 8.

Let us first consider the pulsations illustrated in Fig. 3, as observed with low SO_4 ; two typical examples are shown at high magnification in Fig. 7. The main period divides into two auxiliary periods, B and C, C being generally larger than B. The ratio of B to C appears to be a function of the nature of the carbon.

Let us imagine a carbon electrode in very pure chromic acid, polarised to such a degree that it is completely covered with film, but that there is as yet no evolution of hydrogen. Such being the case, there will be a charge of electrons dammed up behind the film. This is sufficient to draw in the chromic acid at the points, but not at the other positions (Fig. 9c). The current potential is, however, high enough to draw in the finer H_2SO_4 at all positions, and the addition of a small amount of SO_4 to the pure chromic acid will result in dissolution of the whole film. The chromic acid then rushes on to the bared electrode (Fig. 7, oa), with the result that there ensues a sharp pulsation of current and a fall in potential. Owing to the high-current density, formation of the film starts immediately, from the points downwards (Fig. 7, ab). When the

base is reached, the accelerated filming of the plane surface begins (7 *bc*), but this is not completed, because at this stage the potential at the point rises to the "draw-in" value and the diaphragm is again attacked at this position (Fig. 8).

It may be assumed that at this moment a stationary condition exists (as shown in Fig. 8), during which the "jump" potential is opera-

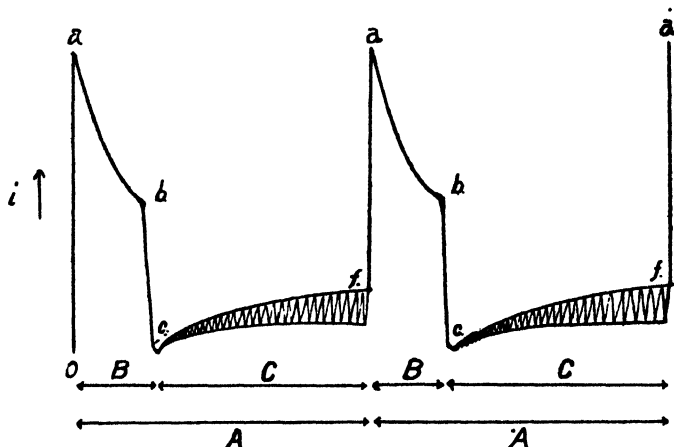


FIG. 7.

tive at *m*, and the "draw-in" potential at *n*. Meanwhile, in a very short space of time, owing to reaction (1), there occurs at the point an impoverishment in hydrogen ions, such that if the film is not too far destroyed (*e.g.*, in low SO_4 solutions) it easily re-forms over the point.

As a result, the potential is raised at the point to the "draw-in" value, but the draw-in cannot at once take place, owing to the lack of H^+ ions, since in the electrostatic absorption process it is first the H^+ ion

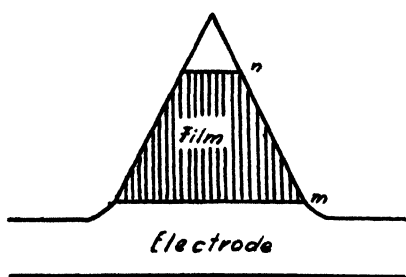


FIG. 8.

which is drawn in and afterwards the HSO_4' (Fig. 9a). Diffusion must first take place, to produce the H^+ ions, and in the interval required for this reaction the current is forced towards *m* (Fig. 8) and the current density there is increased to such a degree that the film grows somewhat. Subsequently, a section at the point is again destroyed, if H^+ has penetrated at *n*, etc., see Fig. 9.

Owing to repeated opening and closing of the points (Fig. 7, *e-f*), the filming process at *m* proceeds by stages (Fig. 8), and when complete covering is attained over the whole of the plane surface, there is a subsequent sudden re-clearing (Fig. 7, *f-a*) and the whole cycle is repeated.

This type of fluctuation can occur, however, only with low SO_4 concentration. In the case of high SO_4 solutions, the surface cleared by draw-in is too great for complete filming to be attained. This type of fluctuation is also absent under conditions of low SO_4 , and high

voltage (below the hydrogen potential). If the formation of the film has progressed from the points as far as the plane surface, when the acceleration sets in the higher voltage will cause a greater piling up of electrons at the point. The "draw-in" potential will therefore extend for a greater distance from the point, and a larger section of the film will be dissolved away, which cannot be re-closed by impoverishment of H^+ ions.

In order to understand the second type of fluctuation, occurring with high SO_4 in the region of the potential corresponding to evolution of hydrogen (Fig. 4 $> d$), the following facts must be taken into consideration:

In the case of current-potential curves taken at platinum cathodes in a 30 per cent. chromic acid solution containing SO_4 , the current i rises with rise of potential π along the line $b-d-f$ (Fig. 10). After passing the hydrogen potential at c , i divides into two sections, i_1 for reduction of $Cr(6)$ to $Cr(3)$ and i_2 for the reaction



the ratio of i_1 to i_2 being that of the shaded to the unshaded areas, both of which are bounded by the axis of the abscissæ and the curve bdf , i.e. the reduction again falls off and eventually ceases. The effect of the

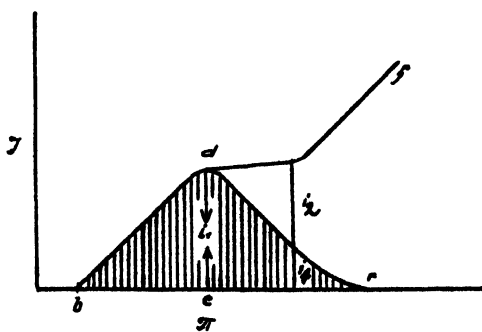


FIG. 10.

foreign ions therefore decreases, in proportion to the increase in discharge of hydrogen ions. The reason for this effect is as follows: The draw-in of H_2SO_4 into the pores of the diaphragm takes place in two stages (see above, Fig. 9 a), and not until the HSO_4' has penetrated to the basic constituent of the molecules of the diaphragm ($Cr(OH)$) can dissolution

of the film take place. If the potential during draw-in is sufficiently high for the draw-in H^+ to be discharged, the degree to which the film will remain undissolved will be regulated by the ability of this reaction to take place more quickly than the HSO_4' can follow.

This type of fluctuation, two examples of which are shown at high magnification in Fig. 11, may be explained as under:—

Let us again imagine a carbon electrode in very pure chromic acid, polarised in this case to a degree which is associated with vigorous

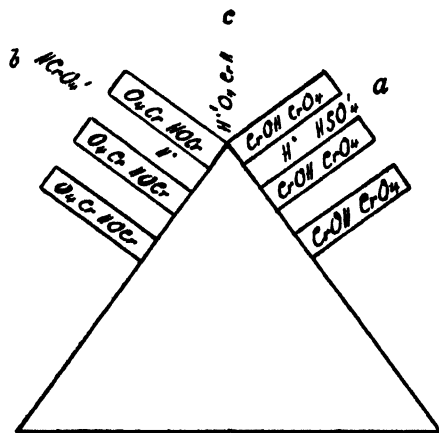


FIG. 9.

evolution of hydrogen. The electrode is then completely covered with film. If, however, the potential prevailing behind the film is everywhere so high that all the H^+ draw-in is discharged, it is immaterial what anions are present in the solution; they will be unable to follow the H^+ sufficiently quickly, and will therefore be incapable of acting as dissolving agents. An addition of SO_4 would, therefore, not affect the conditions in any respect. At voltages well above the H_2 potential, but below the chromium-deposition potential, the only reaction occurring at the filmed

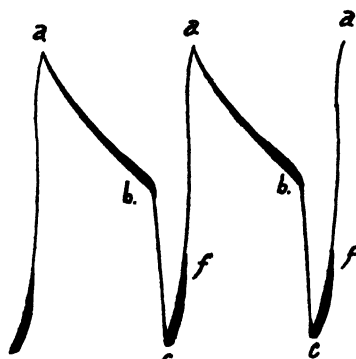


FIG. 11.

electrode is discharge of H^+ ion to H_2 , and there is nothing to cause periodic fluctuations. But if in very pure chromic acid the voltage is so far reduced as to produce *incipient* evolution of H_2 , the addition of SO_4 will result in complete disappearance of the film; the destruction will begin at the regions farthest away from the points, where the "draw-in" (not the H_2) potential is present, and will gradually progress over the points, because the clearing of the remainder of the surface produces over the points a depolarisation below the H_2 potential. The chromic acid rushes on to the bare electrode, and a pulsation of current again occurs (Fig. 11 *c-a*). Next the electrode again becomes filmed, the process beginning at the points and proceeding at a comparatively slow rate from the points to the base (Fig. 11, *a-b*), and then more rapidly on the plane surface (*b-c*). Before the plane surface becomes completely filmed, however, the voltage at the point rises to the potential corresponding to the evolution of hydrogen, whereas at a position nearer the base, it rises only to the "draw-in" potential. This process (Fig. 12) breaks the film from *o* to *n* (approximately) resulting in a fall of current density at *m* to such a value that the growth of the film ceases at this position. A stationary condition would now be anticipated, in which the H_2 potential would be operative at *o*, the "draw-in" potential at *n*, and the "jump" potential at *m*. Meanwhile, over the area *o-n* progressive impoverishment in H^+ ions again takes place, and the current density at *m* is forced up, with resulting growth of the film. At this juncture H^+ penetrates to *o-n*, opening up the film, etc., and there is thus a periodic opening and closing, in this case of a strip (Fig. 11, *c-f*). In the course of these fluctuations the film at *m* grows slightly each time, until, when it reaches the plane surface, there is a sudden completion of the filming and a subsequent equally sudden re-clearing of the electrode, and the cycle is repeated indefinitely.

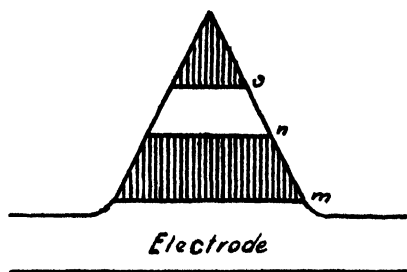


FIG. 12.

With high voltage and high concentration of SO_4 , therefore, the

conditions are similar to those obtaining with low voltage and low SO_4 , because increasing voltage weakens the effect of the foreign ions in proportion as it increases the evolution of hydrogen.

The part played by the film in the electrolysis of aqueous chromic acid solutions at carbon cathodes appears to be very considerably elucidated by the foregoing observations. There is still some difficulty in assessing the significance of the hump m , which occurs on the a - b section of all the potential curves (Figs. 2, 3, 4), and of the horizontal section n - v of the curve in Fig. 4. The latter form indicates that, in spite of increasing voltage, the current density does not continue to increase (so long as there is no evolution of hydrogen), and since the flow of current should be determined only by absorption of HSO_4' , it may be presumed that it is regulated by the rate of diffusion of HSO_4' , which has reached its maximum from n onwards.

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STRUCTURE AND PROPERTIES OF NICKEL DEPOSITED AT HIGH CURRENT DENSITIES.¹

BY WILLIAM BLUM² AND CHARLES KASPER.³

Received 5th February, 1935.

I. Introduction.

During the past fifteen years, the National Bureau of Standards of the United States has co-operated with the Bureau of Engraving and Printing in the development of electrolytic methods for the reproduction of engraved plates used for printing currency (2, 10).⁴ In the process now in use, the initial deposit (or printing face) consists of a nickel layer about 0.25 mm. thick, upon which sufficient iron is deposited to make a finished thickness of about 5 mm. Chromium is subsequently applied to the printing surface. The nickel is deposited at about 2 amp./dm². and the iron at about 7 amp./dm². Under these conditions the total period of deposition is about ninety-six hours.

The occasional need for more rapid deposition, especially in the initial printing of a new series of currency, led to an investigation, that is still in progress, upon the possibility of depositing iron and nickel much more rapidly. This paper is devoted to the structure and mechanical properties of some of the nickel deposits produced in this study. The practical application of very high current densities involves the solution of operating problems that will be discussed in a subsequent publication. All the deposits referred to in this paper are distinctly experimental.

¹ Publication approved by the Director, National Bureau of Standards, Washington, D.C.

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⁴ The numbers in parentheses refer to the bibliography at the end of the paper.

II. Review of Literature.

Much less research has been conducted on the structure of nickel than of copper deposits, and very little upon nickel deposits produced at high current densities. It was early shown by O. P. Watts (1) that nickel can be deposited at much higher current densities than were (or are) used commercially. He obtained "good" deposits at about 30 amp./dm², and in one experiment he applied 95 amp./dm² for one minute and obtained "fine" metal. His deposits were relatively thin (from 0.03 to 0.08 mm.) and he made no quantitative physical measurements.

In 1921, it was reported by W. Blum (3) that nickel deposits from sulphate solutions containing fluoborate were stronger, harder, and less ductile than those from similar solutions containing chloride. The "chloride" deposits had a coarse, conical grain structure, while the "fluoborate" deposits had a fine, fibrous structure.

C. P. Madsen (4) reported that ductile nickel could be produced by lifting the cathode from the bath at frequent intervals. He thereby obtained nickel deposits with a tensile strength of 5000 kg./cm² and a Brinell number of 130, that could be drawn into wires.

In 1925, C. T. Thomas and W. Blum (6) made scratch-hardness measurements on a few nickel deposits produced at relatively low current densities. They found that the hardness was increased by raising the current density or the cathode polarisation; and was decreased by raising the temperature or by using a bath composed entirely of nickel chloride instead of the customary sulphate.

W. M. Phillips (12) reported that an increase in temperature in baths having either a high or a low p_H reduced the scratch-hardness of the deposits.

The most extensive studies upon the structure and properties of nickel deposits have been made in recent years by D. J. Macnaughtan and his associates (5, 7, 8, 11, 13, 14). They determined the effects of adding various substances to nickel sulphate baths and of changing the p_H of the solutions. Most of their deposits were produced at 35° C. at a current density of 1.2 amp./dm². They found that in all of the solutions used, fine-grained, hard deposits were obtained at a high p_H (of 5 to 6), and that the hardest deposits were produced in solutions containing ammonium salts. As the p_H was progressively lowered in solutions containing chlorides, the hardness decreased and then remained nearly constant. In such solutions, potassium salts produced harder deposits. In solutions free from chlorides, as the p_H was lowered, the hardness successively decreased, increased and decreased. In these solutions, potassium salts decreased the hardness.

Macnaughtan (13, 14) and also O'Sullivan (9) concluded that the hardness of nickel deposits is associated with the inclusion of nickel oxide or hydroxide.

III. Scope of this Investigation.

This investigation was devoted to the study of nickel deposits produced at current densities of at least 20 amp./dm². The purpose was to deposit rapidly nickel that is relatively ductile and free from strains. Great hardness or wear resistance is unnecessary, as the printing plates are coated with chromium. Decided roughness is objectionable, as it

causes still more roughness of the iron that is deposited upon the initial layer of nickel. Freedom from pits in the nickel face is important.

IV. Exploratory Experiments.

Commonly accepted theories of nickel deposition indicated that the above requirements might be met with concentrated nickel solutions at a low p_H and a high temperature. To test this prediction, numerous experiments were made upon a small scale, with visual and manual examination of the deposits. The results of these qualitative tests may be summarised as follows.

As the buffer curves of all nickel solutions (except those containing fluorides) have a very steep slope between p_H 5 and 2, it is difficult to maintain a specified p_H between those limits for the long periods required for thick deposits. Practically all the tests were made at a p_H of 2 or less, as it was found that at a p_H of 5 or higher the deposits at very high current densities were cracked and brittle.

The best results were obtained at the boiling-point of the solution (about 102° C.). At this temperature there was no pitting of the deposits in any of the solutions. In baths with a high p_H at high current densities, pitting sometimes occurred almost up to the boiling-point, but in baths with a low p_H , it usually disappeared at about 90° C.

If, as is often assumed, a high concentration of nickel ions is necessary for rapid deposition of nickel, nickel chloride should be superior to the sulphite. It was found, however, that deposits from nickel chloride solutions were invariably more brittle than deposits from sulphate baths with the same p_H . The brittleness of the chloride deposits appeared to increase with current density. Additions of boric acid or of phosphoric acid to buffer the nickel chloride had no pronounced effect. Ammonium chloride increased the hardness (as reported by Macnaughtan for sulphate baths), while calcium chloride had little effect. Fluorides or fluoroborates could not be used in the boiling solutions because a precipitate, probably of nickel oxyfluoride, separated.

Nickel sulphate baths with a p_H of 1 or less yielded relatively soft, ductile nickel deposits at current densities from 10 to 200 amp./dm.², with an apparent increase in ductility as the current density was raised. An increase in the p_H of the solution from 1 to 2 hardened the deposits, while addition of boric acid to the bath softened them. Unsuccessful attempts were made to produce soft nickel from sulphate solutions whose conductivity had been increased by adding various substances. The addition of ammonium sulphate to the bath increased the hardness (as found by Macnaughtan). With sodium sulphate there was not much increase in hardness, but the increase in polarisation offset the increase in conductivity.

The embrittling effect of chloride persisted in baths containing both sulphate and chloride, especially at a low p_H . No difference was found in these qualitative tests, whether commercial nickel salts of good quality or highly purified salts were used. Evidently, the effects of impurities are insignificant in highly acid solutions under these conditions.

V. Quantitative Tests.

1. Preparation for Plating.

A few typical conditions were selected for quantitative measurements. These conditions were limited to those under which fairly smooth, flat deposits about 8 by 20 cm. and 0.6 mm. thick could be produced and separated from the base metal. A further limitation was the capacity of the available generator, namely 250 amperes at 12 volts.

(a) **The Base Metal.**—For each experiment a rectangular polished steel plate 8 by 20 by 0.5 cm., was plated on both sides with an adherent

coating of nickel about 0.025 mm. thick in a regular plating bath,⁶ and was then buffed.

(b) **Separation of the Deposit.**—The hot, acid nickel solutions immediately removed the passive film produced on polished nickel by chromic acid or by anodic treatment in alkali. Even the thin film of graphite that is often used to promote separation was so completely removed by such solutions that the deposits were firmly adherent. The following procedure resulted in deposits that could be separated. The polished nickel surface was rubbed with a graphite suspension, rinsed and then coated with about 0.01 mm. of nickel in the regular nickel bath at about 20°C. and 0.8 amp./dm². The plate was then rinsed and transferred to the hot bath, in which the desired thickness (about 0.6 mm.) was deposited. When the edges of the plate were ground, the deposit could readily be removed from each side. It should be noted that each of the specimens tested was therefore a composite, of which the initial 2 per cent. was deposited from an ordinary nickel bath.

2. Operating Conditions.

(a) **Bath Composition.**—The baths listed in Table II. were prepared from commercial nickel salts without further purification. Chemical

TABLE I.—IMPURITIES IN NICKEL SOLUTIONS.

	4 <i>N</i> Nickel Chloride.		4 <i>N</i> Nickel Sulphate.	
	g./l.	Per cent. of Solid Salt (NiCl ₂ · 6H ₂ O).	g./l.	Per cent. of Solid Salt (NiSO ₄ · 7H ₂ O).
Copper . .	0.030	0.006	0.011	0.002
Iron . .	.005	.001	.006	.001
Lead . .	.010	.002	none	none
Zinc . .	none	none	.006	.001

analysis of the filtered solutions detected only the impurities shown in Table I., in amounts which have also been computed for the solid salts.

The p_H values were determined at

room temperature with a quin-hydrone electrode. They were kept constant during an experiment to within ± 0.1 p_H , except in one sulphate bath (Set 12). This was started at a p_H of 2, but rapidly dropped to 1.6, in spite of additions of nickel hydroxide.

(b) **Anodes.**—Elliptical rolled anodes of so-called "depolarised nickel" were used, with an exposed area slightly larger than that of the cathode. Numerous analyses of similar anodes showed that they contain considerably over 99 per cent. of nickel (plus cobalt), and a small amount of nickel oxide, with less than 0.1 per cent. of copper or 0.25 per cent. of iron. They were surrounded with heavy asbestos bags. They corroded with high efficiency in all the baths except the sulphate bath (Set 12) above referred to. Their rapid consumption caused the liberation in the bags of considerable sludge, which increased the resistance of the bath during the latter part of each run.

(c) **Temperature.**—The temperature was raised to the boiling-point by preliminary passage of current, and was maintained during a run by regulating the amount of asbestos packing around the jars. At the highest current densities, additions of cold water to the bath (replacing the losses by evaporation) were required to prevent too rapid boiling.

(d) **Electrode Spacing.**—The deposition was conducted in 5-liter glass jars, each 12.5 by 17 by 24 cm. deep. The cathode was 5 cm. from each of two anodes. Uniform distribution of the deposit is essential for reliable measurements of tensile strength. By placing glass plates close to each

⁶ This bath contained 1.4*N* NiSO₄, 0.4*N* NiCl₂ and 0.5*M* H₃BO₃, and was operated at p_H 5.3 at 35°C. and 2 amp./dm².

vertical edge of the cathode, the lateral distribution was made nearly uniform, but the deposit was usually about 10 per cent. thicker at the top than at the bottom.

(e) **Cathode Efficiency.**—Accurate measurements of cathode efficiency with a copper coulometer were precluded by the large-sized copper cathode that would be required for the high currents used. Results based on the total weight of the deposit were subject to errors caused by the frequent formation of "trees," some of which dropped off during deposition. The reported efficiencies are based on the measured thicknesses in the reduced sections of the tensile specimens, where approximately the average current density prevailed. The accuracy of the efficiency measurements was probably not better than ± 5 per cent.

3. Methods of Test.

(a) **Tensile Strength and Ductility.**—Two rectangular specimens, 20 by 2 cm., were cut from each deposit after it was removed from the base metal. Each specimen was then machined to produce a reduced section 1.25 cm. wide and 6 cm. long. A number of penciled gage-marks were made at intervals of 1.25 cm. The gage length of 5 cm. that was most nearly symmetrical with the fracture was subsequently selected in measuring the elongation.

Preliminary observations showed that the average thickness computed from the weight of a rectangular specimen agreed within about 1 per cent. with that based on micrometer readings. The latter showed that the thickness towards the top was as much as 10 per cent. greater than that near the bottom, which difference corresponded to an average variation of about 3 per cent. within the gage length. A number of micrometer readings were taken in each reduced section, and the tensile strength was computed from the thickness where fracture occurred rather than from the minimum thickness. These two thicknesses agreed within about 2 per cent. for most of the specimens tested.

The testing machines were chosen to suit the thickness and strength of the specimens. Most of the tests were made on a machine with an adjusted capacity of 900 kg., but a few were made on machines with capacities of 2300 and 270 kg.

(b) **Hardness.**—Four strips were cut from each specimen immediately adjacent to the strips used for tensile tests. Most of the hardness measurements were made upon the back (surface last deposited), which was lightly ground with emery paper to produce a suitably smooth surface. A few tests were made on the front surface, both as deposited and after the initial or starting layer had been ground off. These measurements agreed closely in all cases with those on the back of the deposits.

The Brinell tests were made in a Rockwell Superficial Hardness Tester, in which a ball 1.6 mm. (1/16-inch) in diameter was applied under a load of 15 kg. for 30 seconds. The diameters of the resultant impressions were measured with a micrometer microscope to ± 0.01 mm., which corresponds to a difference of about 7 units in the softer specimens (with about 125 Brinell number) and about 17 units in the harder specimens (with about 225 Brinell number). The results reported in Table II. are the averages of at least six concordant measurements on each deposit, after a very few discordant results had been excluded.

About half of the deposits were also tested in the Vickers Hardness Tester with a square diamond pyramid having a solid angle of 136 degrees. Loads of 10 and 30 kg. were applied, but with the 30 kg. load the indenter nearly penetrated some of the specimens. The results reported in Table II. are based only on a 10 kg. load.

(c) **Structure.**—Two pieces adjacent to the centres of the tensile specimens were cut from each deposit. These were clamped together and the edges were ground flat, polished wet with successively finer abrasives,

TABLE II.—PROPERTIES OF ELECTRODEPOSITED NICKEL.¹

Set No.	Solution.				Current Density, amp./dm ² .	Time, Hr.	Thick-ness, mm.	Cathode efficy, Per Cent.	Ultimate Tensile Strength, kg./cm ² .	Elongation in 5 cm.		Hardness Number.		Structure.		Surface.	
	NiCl ₂ , N.	NiSO ₄ , N.	H ₂ BO ₃ , M.	pH.						Max. Per Cent.	Av. Per Cent.	Brinell.	Vickers.	Type.	Fig.	Type.	Fig.
1	4	—	—	1	22	3	0.54	65	6400	8	8	178	—	fine	1	smooth	3
2	4	—	—	1	30	2	.63	85	7100	8	6	227	201	fine	1	smooth	3
3	4	—	—	1	45	1.6	.72	100	7400	8	7	196	195	fine	1	smooth	3
4	4	—	—	2	30	2	.64	85	6800	7	6	219	—	fine	1	smooth	3
5	4	—	0.7	1	30	2	.64	85	6700	6	6	194	186	fine	1	smooth	3
6	1	3	—	1	30	2	.54	70	6200	18	12	171	172	fine	1	smooth	3
7	1	3	0.7	1	30	2	.54	70	7100	8	8	195	—	fine	1	smooth	3
8	1	4	—	1	22	5	.77	55	4100	24	23	127	—	coarse	2	rough	4
9	—	4	—	1	30	2	.43	55	4400	23	19	123	118	coarse	2	rough	4
10	—	4	—	1	30	3	.63	55	4200	26	25	124	—	coarse	2	rough	4
11	—	4	—	1	42	0.7	.23	65	4800	9	9	122	—	coarse	2	rough	4
12	—	4	—	1.6	30	2	.53	70	4600	5	5	170	—	coarse	2	rough	4
13	—	4	0.7	1	30	3	.66	60	3800	13	13	117	116	coarse	2	rough	4

¹ All deposits were produced at approximately 100° C.

and finished with magnesium oxide on velvet. They were then etched with glacial acetic acid to which just sufficient concentrated nitric acid (less than 1 per cent.) was added to cause attack of the metal. Etching and polishing with magna were repeated until all grinding flow-marks were eliminated. The surface was then wiped with a light mineral oil, which produced more contrast when the structures were photographed, especially at 500 diameters.

VI. Results.

1. Reproducibility and Significance of the Measurements.

(a) Ultimate Tensile Strength.

The results with two specimens cut from the same deposit invariably agreed within 3 per cent. Specimens from similar deposits produced in separate runs agreed within about 5 per cent. The results reported in Table II. are the averages of at least two, and usually four, specimens, with no results excluded.

(b) Elongation.

Most of the specimens had at least a few visible nodules on the surface. In general (Table II.), there were more nodules on the de-

posits from sulphate than from chloride baths. An effort was made to cut each specimen so that none of these nodules were at the edges of the reduced section. However, it was evident that, as shown in Figs. 3† and 4†, fracture often occurred where a nodule was present. The very good reproducibility of the tensile tests indicates that the nodules had no marked effect on the tensile strength. However, the presence of nodules undoubtedly reduced the ductility and led to less concordant results for the elongation. As the nodules would always tend to decrease the elongation, the maximum values in Table II. probably represent more truly the ductility of the metal than do the average values.

(c) **Hardness.**—In almost every case, the Brinell and Vickers numbers agreed within the probable accuracy of the measurements.

(d) **Structure.**—The structure of two or more pieces of each deposit were so similar that any one of them could be considered typical. The structures are of two principal types, represented by Figs. 1* and 2*.

2. Effects of Each Variable.

(a) **Chloride versus Sulphate.**—The data reported in Table II. show that the deposits are in two widely different classes. Those obtained from nickel chloride solutions have a fine-grained structure and are relatively smooth, strong, hard and brittle, while the corresponding deposits from the sulphate baths are rough, coarse-grained, soft and ductile. The presence of only 25 per cent. of nickel chloride in the sulphate baths (Sets 6 and 7) makes the deposits almost the same as those from pure chloride solutions. This is the one outstanding conclusion of this study, and fully confirms the preliminary qualitative tests.

(b) **Current Density.**—It is more difficult to determine which other variables had definite effects. Comparison of the tensile strengths in Sets 1, 2, and 3 indicates a small increase as the current density was raised, with no corresponding change in elongation. Sets 1 and 2 show an increase in Brinell number, which, however, is not continued into Set 3.

In the sulphate solutions the apparent effect of current density in increasing the tensile strength may not be definite, as the deposits (Sets 8, 9, 10 and 11) are not of the same thickness. The greater strength and lower ductility of Set 11 are partly due to the lesser thickness of these specimens. As is evident in Fig. 2A,* the first part of each deposit (especially of those with coarse crystals) is finer-grained and presumably stronger than the part deposited later. It was necessary to use thin specimens for Set 11 because the maximum available voltage was required for this high-current density in the sulphate bath, and, in less than one hour's operation, the accumulation of sludge in the anode bags increased the resistance and reduced the current density below that specified. There is no perceptible effect of current density on the Brinell hardness, which is apparently less affected than is the tensile strength by the thickness of the deposits.

(c) **pH.**—Comparison of Sets 2 and 4 shows that a change in pH from 1 to 2 has no definite effect in chloride solutions. Sets 9 and 12 show, however, that in sulphate solutions an increase in pH from 1 to 1.6 (or initially to 2), reduces the ductility and increases the Brinell hardness.

(d) **Boric Acid.**—Comparison of Sets 2 and 5 shows that the addition

* Plate XLVII.

† Plate XLVIII.

of boric acid (sufficient to saturate the solution at room temperature) had no pronounced effect on the deposits in chloride solutions; while Sets 9 and 13 indicate a slight softening effect in the sulphate baths.

(e) **Cathode Efficiency.**—The approximate values show that the efficiency was always higher in chloride solutions than in corresponding sulphate baths. In the former solutions it increased decidedly with current density, but only slightly in the sulphate baths.

VII. Conclusions.

The most obvious conclusion of this investigation is the need for more exhaustive study of the deposition of nickel (and of other metals) over a very wide range of conditions before any complete theory of metal deposition can be developed. The need is also shown for more discriminating methods of examining deposits than the conventional metallographic and mechanical methods. It is hoped that the applications of X-rays and electron diffraction, to be discussed in this symposium, will help to meet this need.

Pending a more detailed study, including the range between the normal conditions and the extreme conditions here used, it would be futile to attempt to explain the above results. The difficulty of formulating a complete theory is emphasised by the wide difference in the relative effects of chloride and sulphate ions under different conditions. It was found by Thomas and Blum (6) and by Macnaughtan, Gardam and Hammand (13) that at low temperatures and current densities, the presence of chlorides made softer deposits (which is consistent with the general experience of practical platers). However, at the high temperature and current density used in this work, the presence of chloride always resulted in harder deposits. It is obvious that any theory such as that advanced by Macnaughtan (13) to explain the softening effect of chloride ions would require radical modification to include the hardening effect here reported. Discussion of this and other possible theories will therefore be reserved until more data are available.

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CONTRIBUTION TO THE EXPERIMENTAL STUDY OF THE INFLUENCE OF THE SUPPORT OR CATHODE ON THE STRUCTURE OF ELECTROLYTIC DEPOSITS OBTAINED IN AQUEOUS SOLUTION.

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As in the phenomena of solidification and generally of phase change, the structural formation of electrolytic deposits depends on two fundamental quantities:

(1) *The rate of inception* N_G of the zones or crystalline centres, *i.e.*, the number of centres brought into being in unit time per unit volume (or surface); this is the *KZ* (*Kern Zahl*) mentioned in German literature.

(2) *Rate of growth* V_G ; the rate of increase or displacement of the limits of the crystal: this is the *KG* (*Kristallisation Geschwindigkeit*) of the German notation. It is indeed a vectorial quantity which may be variable according to the direction. Thus, Glazunov¹ distinguishes a linear rate normal to the surface of the cathode KG_1 (or V_{O_1}) and a rate parallel to its surface KG_{11} (or $V_{O_{11}}$) or, more exactly, rates parallel and normal to the lines of electric force, the main growth following the direction of these lines of force.²

From these two quantities are derived the three structural characteristics: the *fineness, orientation and form* of the crystals forming the electrodeposit; in particular, the fineness increases with N_G and decreases with V_G .

These two quantities depend upon:

(a) The conditions outside the cathode or support on which the deposit is formed;

(b) The support or cathode itself.

(a) The external conditions are manifold: current density, temperature, concentration of metal ions and its variation in the course of the electrolysis, acidity or p_H , stirring of the liquid, presence of colloids, of passivating agents, of polyvalent ions, etc. These various factors serve

¹ Glazunov and Janousek: *KZ, KG_1 et KG_{11} pendant la formation du dépôt cathodique*. 12ème Congrès de Chimie Industrielle, Octobre, 1932.

² Glazunov and Rada, *Relation existant entre la direction d'accroissement du dépôt cathodique et la forme des lignes de force électrique*. 12ème Congrès de Chimie Industrielle, Octobre, 1932.

to increase or diminish either N_O or V_O , and to modify thereby the fine structure of the deposit. The more important factors in this respect are temperature, concentration and current density.

(b) The support of the deposit, base metal or cathode, may affect the structure of the deposit directly or indirectly by modifying the above-mentioned external factors, as by changing the current density, the concentration and the displacement of the contact electrolyte, etc.

This effect of the support (which we envisage here as due to external factors) has already been the object of a great deal of work.³ On the other hand, the cathode and the preparation of its surface may affect the structure of the electrodeposit.

We have indicated elsewhere⁴ the rôle of the structure on the quality, *i.e.*, on the specific properties and the defects of electrodeposits.

This influence of the support or cathode depends on its condition envisaged under the following triple aspect:

A.—*Geometrical condition of the surface.*

B.—*Nature and chemical condition.*

C.—*Crystalline condition.*

A.—*Geometrical condition of the surface* (and modification of this condition in the course of deposition).

The linear rate of crystallisation V_O is at a maximum along the lines of electric force, which at first impinge on the cathode normally to a plane tangent to the surface. The crystals tend to develop and to orient themselves along lines orthogonal to the surface (Fig. 1*); to oblique and lateral development, there is, moreover, opposed the material obstacle of the neighbouring crystals as well as the impoverishment of the intercrystalline liquid.

Modifications of the chemical composition, of the concentration of metal ions and of the contact p_H of the crystals are counterbalanced by the movements or displacements of the liquid along the surface of the cathode arising either from artificial or natural agitation or from convection currents resulting from the diminished density of the layer of electrolyte in the neighbourhood of the cathode, which leads to a continuous changing of the layer. These liquid movements tend to the homogenisation of the electrolyte, a tendency which is retarded or perturbed by the form, and the vertical or horizontal position of the cathode, by the irregularities of the surface as well as by the gaseous bubbles which may adhere to it. There results a heterogeneity of concentration of the electrolyte which acts on the distribution of the current density, which is greater at regions of large than at regions of small concentration, and may become zero in certain cases. This indirect effect of the configuration and the position of the cathodic surface is superposed on its direct effect on the current density.

In addition to this, the local impoverishment in metal or hydrogen ions may go so far as to bring about the precipitation of hydrates (Figs. 3, 4 and 8*). Moreover, Cr deposits often contain hydrates, the presence of which may be proved by means of oxygen dosages. Thus we found a total oxygen percentage of 0.2 by reduction with carbon *in vacuo*, the hydrogen percentage being, on the other hand, 0.029.

Since N_O depends also on the concentration and on the current density, it would seem that the structure is modified for these reasons by

³ Billiter, Hothersall, MacNaughtan, Gardam and Hammond, etc.

⁴ A. Portevin and M. Cymboliste, *Rev. Met.*, 1933, 30, 323.

* Plates XLIX-LII.

curvature of the surface in respect of fine structure and the development of crystals. Thus, scratches on the polished surface may determine the *exclusive* formation of centres of crystallisation, as shown by A. Glazunov and S. Janousek in the electrolysis of copper sulphate.⁵ These crystals multiply and grow from germs, each point bringing about a bundle or fan (Figs. 6 and 7 *) of divergent elongated crystals which expand like sphero-crystals, giving an external surface with a larger radius of curvature and with greater development (Fig. 2 *).

The number of these points per unit of cathode surface and the value of B_0 determine whether pitting of the external surface of the deposit will be accentuated or not; the progression the one towards the other of these kinds of sphero-crystals may temporarily bring about cavities (Figs. 12 and 14 *).

Inversely, the initial cavities of the cathode or these new temporary cavities on the surface of the deposit tend to close up by convergence of the crystalline groups (Figs. 10 and 11), of which the residual liquid has a small metal and hydrogen-ion concentration, leading in all the liquid regions thus immobilised to the deposition of hydrate at the junctions of the crystals or beneath the gaseous bubbles (Fig. 4 *).

Each break in the profile of the surface, whether a projecting (Fig. 5 *) or a re-entrant angle (Figs. 8 * and 9), is the point whence there arises a "joint" which can become filled with hydrate (Fig. 8 *).

To these irregularities of the cathode are added those formed by the solid particles deposited by cataphoresis which, if they are conductors, form independent centres of crystallisation, whence arises the importance of a bath which is optically clean and has no precipitate of hydrates.

There is thus, in the course of the deposition, a *geometric modification of the surface* on which the metal is deposited, and this may lead to amplification or attenuation of the initial of temporary pittings.

The degree of polish of the cathodic surface depends on its mechanical and chemical preparation, as well as on the actual nature of the cathode support, *i.e.*, according to whether it is homogeneous or not (see paragraph B) and on its physical defects: holes or fissures of the material forming the cathode.

In order to facilitate the growth of the deposit, the preparation of the surface is often so conducted as to bring about irregularities and unevenness by energetic sand-papering or scouring. See, for example:

- (1) *Reliefs* brought about by machining (Fig. 5 *), or by scouring (Figs. 6 and 7 *).
- (2) Hollows or cavities resulting from machining (Fig. 8 *), or scouring (Figs. 10 and 11 *). Growth of crystalline groups (Figs. 12 * and 14). Cracks due to irregularities of tempering (Fig. 13 *).

These photographs show clearly the perturbations in the structure of the electrodeposit and the physical defects which accompany them.

The layer of initial fine crystallisation which is noticeable in industrial electrolytic deposits is analogous to the minute zone of very fine crystals formed in the solidification of a liquid metal (or the condensation of a metallic vapour) on contact with a cold metallic surface. From this fine layer there flow crystals, which are elongated and oriented, according to the line of flow of the electricity in the first case, and of the heat in the second case. Thus, the main structure of the electrodeposit is analogous to the basaltic zone or the zone of transcrystallisation of cast metals (or of metals obtained by sublimation against a cooled surface), although in the latter

⁵ *Chemických listy*, XXVII, fasc. 23.

* Plates XLIX-LIII.

case there is no tendency to the formation of fanlike crystalline groups such as we have mentioned.

B.—*Chemical Nature and Condition.*

Two principal cases are to be distinguished:

- (1) The surface of the cathode is of the same metal as that which is to be deposited; *e.g.*, electrolytic refining, or when the cathode is given a preliminary coating.
- (2) The metal of the cathode is different from that which is to be deposited. In this case, which applies generally to all electrolytic protective coatings, there is the possibility of chemical reaction between the cathode and the electrolyte.

The surface of the cathode may be modified chemically:

Either during the preparation of the surface by polishing, scouring, or washing. During these operations, there may be:

(a) Oxidation of the surface: we know that for many industrial metals (iron, aluminium, etc.) simple exposure to air determines the formation of an oxide film (U. Evans). This oxidation is naturally accelerated by the superficial increase in temperature during polishing, by washing and by transport in air of humid pieces.

(b) Selective solution of the cathode in scouring: the different constituents are unequally attacked, the less reactive protruding on the surface (*e.g.*, graphite (Fig. 17), and the phosphorous eutectic (Fig. 16 *) of steel), then, when they are detached, giving rise to a layer or deposit. Furthermore, the attack on solid solutions also is selective, leaving powdery residues (*e.g.*, the attack of sulphuric acid on brass, with preferential solution of zinc, of various acids on steels, leaving carbon, etc.). Finally, the metallic inclusions may be partially liberated.

(c) Final reaction of the scouring agent on the metal or alloy—either by foreign matters due to:

Insufficient degreasing (see *e.g.*, the experiments of Marie and Thon on the structure of deposits on cathodes provided with insulating layers);⁶ or to Adsorbed colloids.⁷

By displacement of the metal by reaction with the electrolyte; or
By the presence, at the surface, of solid conducting particles deposited by cataphoresis, or non-conducting gaseous particles, *i.e.*, bubbles.

The latter act, as we have said, to modify the circulation of the liquid at the surface and also serve as centres of crystallisation, whence arises the radial crystallisation observed around the particles and bubbles (Fig. 18 *); all this brings about the small physical defects which we have studied elsewhere.⁸

Micelles of colloidal substances analogously serve as centres (rise of N_C) and increase the viscosity of the contact electrolyte (diminution of V_C), which brings about numerous fine crystals, which, however, do not possess good mechanical properties.

Oxydation of the surface, either during its preparation or during electrolysis, may play an important part, for it is one of the reasons suggested as an explanation of the passivity of metals (either the formation of a layer of oxide or dissolution of oxygen in the superficial layer). We know that all oxidising agents added to the bath are passivators, whilst all reducing agents are activators (*i.e.*, they re-establish the potential).

* Plate LIV.

⁶ *J. Chimie Physique*, 1932, 29, 569.

⁷ Jacquet, *C.R. Acad. Sci.*, 1933, 195, 921.

⁸ A. Portevin et M. Cymboliste, *loc. cit.*

The structure of the deposit depends on the *initial* values of N_0 and V_0 , which are themselves dependent not on the general characteristics of the bath (concentration of electrolyte, temperature, current density), but on the values of these characteristics at the points of contact between electrolyte and cathode, so that the initial values (and therefore the structure) of N_0 and V_0 may be modified by first immersing the cathode either in a colloidal solution or in a concentrated solution, which provides an initial increase of concentration of metallic ions (Billiter).

C.—Crystalline Structure of the Cathode.

In principle, each crystal started on the surface of the cathode is a germ or centre of crystallisation if it is identical or isomorphous with the deposit which is forming and, in any case, it can serve to orient the crystals which are deposited.

This fact is general and natural for the growth of crystals, whether by solidification, by condensation of vapour, or by electrolytic precipitation, *e.g.*, examples of crystalline continuity between the support and the deposit.

The influence of the crystalline structure of the base metal on that of the electrolytic deposit has been often studied; stated first by Huntington,⁹ then by Hogaboom,¹⁰ it was denied by Sand and Hughes,¹¹ proved and studied by Blum and Rawdon,¹² Kenneth Graham,¹³ Hothersall,¹⁴ Billiter,¹⁵ Hunt,¹⁶ etc.

It is evident that the development and the growth of crystals in the thickness of the deposit exhibit the influence of those crystals on the metallic ions of the metal being deposited and, if a new layer is deposited, there is a crystalline continuity; this influence has been proved in the case of cast or rolled and annealed copper on which a layer of copper is deposited in an acid bath when there has been a preliminary scouring with nitric acid to take off the polished skin and expose the crystals.

If the cathode is scoured in an alkaline medium, this phenomenon does not appear, either because, by reason of the polishing, there is a hardened, almost amorphous, layer of metal, or by reason of the interposition of foreign matter, *e.g.*, a layer of hydrogen, oxygen, oxide, etc.

It has been known since the work of Osmond¹⁷ that polishing creates on the surface of the metal a hardened skin which Beilby¹⁸ likened to an amorphous state, and which must be removed by chemical attack if one desires to observe the true crystalline structure of the metal. Hothersall has proved its influence in his study upon the adherence of deposits on brass;¹⁹ here, again, it is necessary to dissolve (chemically by acid, or

⁹ *Trans. Faraday Soc.* 1915, 1, 324.

¹⁰ G. B. Hogaboom, *Trans. Amer. Electrochem. Soc.*, 1916, 29, 369, and discussion on report by Blum, *Trans. Amer. Electrochem. Soc.*, 1921, 40, 318.

¹¹ H. J. S. Sand, *Fourth Report on Colloid Chemistry*, Brit. Ass., London, 1922, 353; W. H. Hughes, *Bull.* 6, D.S.I.R., London, 1922, 36.

¹² W. Blum and H. S. Rawdon, *Trans. Amer. Electrochem. Soc.*, 1923, 44, 305.

¹³ A. Kenneth Graham, *Trans. Amer. Electrochem. Soc.*, 1923, 44, 427.

¹⁴ A. W. Hothersall, *Electroplaters' and Depositors' Technical Society*, 18th March, 1931; *Metal Industry*, 1st., February, 1935.

¹⁵ J. Billiter, *Prinzipien der Galvanotechnik*, Springer, Vienne, 1934.

¹⁶ L. B. Hunt, *J. Physic. Chemistry*, 1932, 36, 1006.

¹⁷ Osmond and Cartaud, *Les enseignements scientifiques du polissage*, *Rev. gen. Sci.*, 1905, 16.

¹⁸ Beilby, *Phil. Mag.*, 1904, (6), 8, 258.

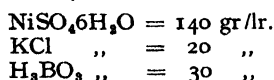
¹⁹ A. W. Hothersall, "The Adhesion of Electrodeposited Nickel to Brass," *J. Electrodeposits. Technical. Soc.*, 1932, 7, 115.

electrolytically) this amorphous skin in order to maintain the reticular orientation of the base metal in the electrodeposit.

This tendency towards the reproduction of the crystalline structure of the support leads naturally to strong adherence of the deposit by reason of the reticular contact which results. This adherence was demonstrated by Skowronski in the electrolytic refining of copper at Anaconda, where the plates on which the refined metal is to be received are obtained by electrodeposition on sheets of copper.

This crystalline continuity was also demonstrated by Hothersall²⁰ in the electrodeposition of nickel on electrodeposited nickel,²¹ but he could not show it with certainty in the case of nickel electrodeposited on cast or rolled nickel; the revelation of structures by attack is, moreover, more difficult in this case than in that of copper.

It appears clearly, however, from the results shown in Figs. 19, 20 and 21 * (obtained in a nickel bath,



at p_H 4.5, and temperature 35°C. , D.C. = 1 amp./dm.² on a nickel cathode cast after scouring in a boiling solution of 10 per cent. ammonium persulphate, followed by anodic cleaning in the nickel bath), that the crystallisation of the deposit is very fully primed with crystals of the base metal, but this initial and local effect is then masked by the general, fibrous, oriented structure of the electrodeposits, and, moreover, the continuity is much less striking than in such examples as that of copper on a laminated copper cathode.

We have, moreover, shown in the case of copper that the crystalline continuity of the superposed deposits of copper obtained in the same conditions of electrolysis can be traced even across thin interposed layers of electrolytic nickel, so long as these interposed layers do not exceed a certain thickness.²²

Similarly, according to P. Jacquet,²³ the crystalline continuity of the base metal in the deposit is prevented in the case of copper by a thin layer of hydrophilic colloid (proteins and peptones) except when the support consists of electrolytic copper. In this way successive electrodeposits of copper separated by a thin adsorption layer of serum, albumen or of peptone, exhibit crystalline continuity.

On the other hand, this continuity between different successive electrodeposits cannot be manifested if one or the other of the conditions of electrolysis (temperature, current density . . .) is changed, thereby modifying N_C .²⁴

Any important variation in the current density, however, leads to a correspondingly clear demarcation in the deposit without any necessity to interrupt the current (Billiter).

As for the crystalline continuity at the junction of different metals, even of identical lattice, or very nearly so (such as copper and nickel, or, better still, gold and silver), no micrographic example has been published.

²⁰ A. W. Hothersall, "The Adhesion of Electrodeposited Coatings to Steel," *Trans. Amer. Electrochem. Soc.*, 1933, 74, 69.

²¹ In the same way Kohlschutter has shown the crystalline influence which successive electrolytic deposits of silver exercise on one another.

²² Figs. 39 to 42, page 338, of the *Revue de Métallurgie*, 1933, 30.

²³ P. Jacquet, *C.R.*, 1935, 200, 226.

²⁴ See, e.g., Fig. 63, p. 344, *Revue de Métallurgie*, 1933.

* Plate LV.

It should be said that in this case the superficial chemical effect of the cleaning of which we have spoken, increases the difficulties of realising the effect.

On the other hand, Foerster,²⁵ has found a very sharp crystalline influence of an electrolytic layer of tin on the ulterior electrodeposition of this metal. He has demonstrated the crystalline continuity of cadmium and of zinc on cathodes cast from these metals and has even succeeded in making cadmium grow on tin and tin on lead, although these metals are of different crystalline systems. It is convenient to recall here that amongst the natural minerals one finds very plain associations, and well-defined orientations between crystals of quite different systems (calcite with quartz and with mica), as well as in crystallising salts on the surface of other crystals.

Wood,²⁶ by X-ray study, has shown the influence of the crystalline orientation of a copper cathode on electrodeposits of nickel obtained with current densities exceeding 60 milliamperes/cm.². We have, moreover, in experiments now being conducted, shown micrographically indications of orientation of the deposit of nickel on a copper cathode.

To sum up, it appears that the effect of crystalline continuity between the cathode support and the electrodeposit depends upon :—

(a) *Contact between the electrolyte and the cathode*, requiring the absence of interposition of foreign matters and the elimination of the hardened amorphous layer due to polishing ;

(b) *The value of N_C* . If N_C is large (fine structure of the deposit) in comparison with the number ϵ of crystals of the cathode per unit of surface, the effect of the surface is nil, ϵ being negligible in regard to N_C . On the other hand, if N_C is zero, or very small, c is ϵ , which determines the fine structure and the crystallisation of the deposit.

We may conclude from this that crystalline continuity of the cathode deposit is of *rare* occurrence. Examples have been given by various authors and by ourselves for copper. For nickel, by reason of the high value of N_C of the usual nickel baths, it has only been observed for base metals which have been electro-deposited, but the micrographs of Figs. 19, 20, 21 * and 23 † give examples in which we can see an influence of certain grains of the cast nickel cathode on the crystallisation of the electrodeposit.

Finally, mention must be made of the influence of the other characteristic quantity of crystallisation : the linear rate of crystallisation V_C . Inside the electrodeposits, where such a rate is at a maximum along the current lines, the crystals stretch themselves normally to the cathodic surface along a privileged crystallographic direction and so it is also into the basaltic zone of melted metals where the dendrites stretch and orient themselves along a quaternary axis of the cube. Consequently, the chances of crystalline continuities with the crystals of the base metal are thus at a maximum when these crystals have an orientation akin to the privileged one ; and this fact explains why :—

(1) In industrial deposits of rapid crystallisation—as in the case of nickel deposits—the continuity is proved only for some grains of the base metal (see Figs. 19 to 21 *) ;

(2) The continuity is more easily observed—and even sometimes exclusively so—when the base metal is itself a preliminary electrodeposit, the crystals of which have, all of them, the privileged orientation.

²⁵ *Z. Electrochem.*, 1926, **32**, 525.

²⁶ W. A. Wood, *Proc. Phys. Soc.*, 1931, **43**, 138.

* Plate LV.

† Plate LVI.

Summary.

The fine structure of electrodeposits may be influenced by the crystallisation of the cathode and especially the fine structure (or number N of crystals per unit surface) of the cathode, and, on the other hand, depends upon N_0 and V_0 , which are functions of the concentration of the contact electrolyte, the current density and the temperature.

Whether or not there is a marked influence of the crystallisation of the cathode depends upon the relation between N and N_0 .

It is not surprising that, whether this influence of the base metal exists or not, depends upon whether one changes for example the nature of the electrolytic bath and the current density.

GENERAL DISCUSSION.

Dr. S. Glasstone (*Sheffield*) said: It is becoming increasingly evident from recent studies of electrodeposition and from the group of papers now being discussed that the formation of a smooth micro-crystalline deposit of a metal on the cathode is always to be accounted for by the presence of finely-divided material, possibly colloidal in nature, which interferes with crystal growth. In the deposition of nickel, and of similar metals, this evidently consists of hydroxide or hydrated oxide, or perhaps of basic salt, as the work of Macnaughtan and Hothersall, and of others, has shewn, and the formation of such compounds as a result of the decrease of hydrogen ion concentration in the immediate vicinity of the cathode is easy to understand. With silver, however, which is obtained in a fine-grained form from argentocyanide solutions, the nature of the pseudo-colloidal matter is not so obvious; in the presence of excess of free cyanide it appears improbable that this would be silver cyanide, and as long ago as 1913 Kohlschütter¹ suggested that a silver sub-cyanide, similar in constitution to the so-called photo-halides, was formed on the cathode and prevented the growth of metal crystals. About five years ago, when considering the mechanism of the deposition of silver from argentocyanide solutions it was suggested,² partly in order to account for the ready deposition from solution containing so few individual silver ions and partly to explain the physical nature of the deposits, that cations of the type Ag_2CN^+ , and not simple Ag^+ ions, are actually discharged at the cathode. That such complex positive ions probably exist is shown by the existence of the salts 2AgNO_3 , AgCN and 2AgNO_3 , AgI , by the solubility of silver cyanide and iodide in silver nitrate solutions, and by transport experiments.³ When the ion Ag_2CN^+ is discharged, the resulting radical immediately decomposes giving silver and silver cyanide, the latter providing *in situ* the necessary material for preventing growth of the silver crystals. Professor Schlötter has stated that his electro-deposits of silver from iodide solutions contained considerable amounts of silver iodide, and if it is supposed that complex cations, such as Ag_2I^+ , the existence of which appears highly probable from the work of Hellwig,³ are discharged at the cathode the observations can be readily explained. The presence of similar positive complexes in cuprocyanide solutions⁴ would account for the

¹ *Z. Elektrochem.*, 1913, 19, 181.

² Glasstone, *J. Chem. Soc.*, 1929, 692.

³ Hellwig, *Z. anorg. Chem.*, 1900, 25, 157.

⁴ Glasstone, *J. Chem. Soc.*, 1929, 702.

fact, noted by Macnaughtan and Hotherhall, that non-metallic matter is definitely included in copper deposited from such solutions.

Two subjects of a different nature which arise from Dr. Blum's paper are worthy of comment. In a subsequent contribution to this Discussion⁵ the incorrectness of the view, widely held at one time, that fine-grained deposits are associated with an appreciable irreversibility of deposition is emphasised, and further evidence is available from the work of Blum and Kasper. The nickel deposits from boiling solutions are as fine-grained and as hard as those normally obtained at ordinary temperatures; in the former case the nickel is deposited almost reversibly but in the latter there is considerable irreversibility. The second point refers to the question of the maximum *C.D.* at which nickel can theoretically be deposited in a coherent form, that is without the collateral evolution of large amounts of hydrogen; the limiting *C.D.* for a *N*-solution at room temperatures, according to a simple formula recently published,⁶ is about 2.7 amp./dm.², and so for the 4*N*-solutions used by Blum and Kasper at about 100°, the limiting *C.D.* should be of the order of 50 amp./dm.² In private conversation Dr. Blum has pointed out that the solutions were being agitated as a result of ebullition, so that the maximum *C.D.* might be raised to 100 amp./dm.², and in fact *C.D.*'s of this order had been used in preliminary work and had proved satisfactory. Although the limiting *C.D.* formula mentioned can only be regarded as approximate it might prove useful to the practical electro-depositor as an indication of the maximum *C.D.*'s which might be employed with reasonable hopes of satisfactory results. It is of interest in this connection to note that in a paper contributed by Wernick to a later part of the Discussion, it is stated that good deposits were obtained from unstirred cyanide solutions containing 30 g./litre of cadmium at *C.D.*'s up to 15 amp./ft.², whereas at 30 amp./ft.² "burnt" deposits resulted; the limiting *C.D.* in the solutions used may be calculated as 15 amp./ft.² in excellent agreement with the observations. With stirred solutions higher *C.D.*'s could naturally be used with success.

Mr. A. W. Hotherhall (*London*) said: The general theory advanced by Macnaughtan, Gardam and Hammond, and referred to briefly in the contribution to this Discussion by Macnaughtan and myself, was intended to form the basis upon which a comprehensive explanation of the mechanism of nickel deposition could be built and it was fully anticipated that as fresh data became available an expansion of this theory would be necessary. Some recent, unpublished results obtained at Woolwich confirms the authors' findings; thus, deposits prepared from a solution containing nickel chloride and boric acid have been found to be harder under similar conditions of deposition than from a solution containing nickel sulphate, boric acid and a small concentration of chloride. At 35° C. therefore, the addition of a small concentration of chloride to a sulphate solution results in a softening of the deposit within a certain range of p_H and current density, whilst both at 35° C. and 100° C. and over a wider range of p_H and current density, a large concentration of chloride produces a harder deposit. Further it has been found that increase of current density in the sulphate, boric acid type of solution produces a progressive increase

⁵ This vol., p. 1232.

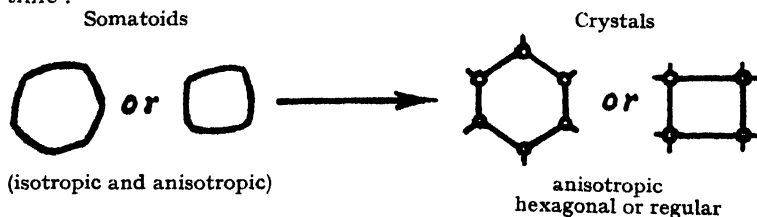
⁶ Glasstone, *Trans. Electrochem. Soc.*, 1931, 59, 277.

in the hardness at 35° C., but a decrease at 100° C. More data are required to shew in what way large changes of chloride concentration, current density and temperature affect the amount of colloidal material available at the cathode face but, so far, no result has emerged from any of these data to disturb the general hypothesis that it is the amount and condition of the nickel hydroxide formed at the cathode face which determines the properties and structure of the deposit. Nor is it established that any modification is required of the theory as to the softening effect of small concentrations of chloride ions.

The general relationship shewn in the authors' results between Brinell hardness number and tensile strength is in good agreement with results published by Gardam and Macnaughtan and further confirms the usefulness of the Brinell hardness number as a quantitative measure of the mechanical properties of nickel deposits.

The minimum Brinell hardness number of the deposits obtained in the authors' experiments is similar to that obtained at Woolwich under conditions widely different as regards composition of solution, temperature, current density and acidity (see Table I, Macnaughtan and Hothersall),⁷ and is considerably above the hardness of the fully A more *general* significance of our experiments consists in the possibility they offer of gaining some knowledge of the *conditions prevailing in the cathodic film* by using *morphological methods*. The structure of the cathodic film is a most important question in all kinds of electrolytic processes, and our knowledge of it is, so far, very meagre indeed. The somatoid structure observed in a deposit gives evidence of the conditions existing on the surface of the cathode and in the cathodic film during the electrolysis. The somatoid formations in the metal reveal the discontinuities (of distribution of matter, or of the conditions of space, time or energy) which existed in the cathodic space and which otherwise it would be difficult to recognise. Even in the cases where no such discontinuities are revealed by some coarse somatoid deposit, we must reckon with the possibility of their existence. The more or less continuous series of phenomena leading from the coarse deposits of obviously somatoid character to the finer effects of colloidal substances on the properties of electrochemical deposits permit us to make extrapolations in this direction.

H. Reininger (*Leipzig*) said: The somatoids described to us by Professor Kohlschütter are very interesting bodies from the point of view of crystallography. They obviously represent a preliminary stage in the formation of tridimensionally periodic, orientated, anisotropic bodies. Their fine structure bears a great resemblance to that of the "liquid crystals" of Lehmann, and the *Fastkristalle* ("almost-crystals") of Rinne and Schiebold. The somatoids must be regarded as unstable "mixed" structures (composed of isotropic and anisotropic material), with a tendency to become perfectly crystalline in the course of time:



⁷ This vol., page 1173.

Transformation of this kind must be accompanied by form changes, and thus produce internal strains, adversely affecting the hardness and resistivity of metallic deposits.

Dr. L. Tronstad (*Trondheim*) said: I should like to call attention to a recent important paper by T. Erdey-Grúz,⁸ dealing with the electrolytic growth of single crystals of silver, and in which the new aspects of crystal growth and over-voltage, etc., according to Kossel, Stranski, Volmer, etc., are discussed. The presence of a "cathodic film" (oxide?) has been found to affect the process of cathodic crystallisation considerably.

Dr. E. Liebreich (*Berlin-Halensee*) said: With regard to the observation of Professor Schlötter that hydrogen is absorbed to a remarkable extent under the film of silver iodide, may I remind the meeting that iron, if covered with a film of bivalent iron hydroxide, still absorbs hydrogen in large amounts, as I was able to show a few years ago.

Professor Schlötter points out that the hydrogen over-voltage will be influenced by the anions. This influence is known and quite true. But it has been neglected always as much as possible by physical investigators, since according to their theory the over-voltage is said to be independent of the constitution of the solution. We therefore quarrel with physicists. Nevertheless I think the day will come when we shall regard over-voltage as rather a chemical than a physical phenomenon.

I would like to discuss another point. Yesterday we discussed the possibility of finding metal-surfaces, which are really clean and are not covered with any layer. It seems to me that this possibility may arise under certain circumstances on cathodic polarisation, if the current density is maintained within certain limits. If we plot the cathode potential against the voltage between two points of the electric arrangement which are uninfluenced by the changes of the resistance on the surface of the cathode instead of against the current, we can observe all changes in the cathode potential. If we do not so the co-operation of the decrease of the current and the ennobling of the potential will efface the real chngement of the cathodic potential and lead to a new point on the curve which lies a little lower as before. Using this method it can be shown that there exists a period where hydrogen is developed by a very small density of current, but disappears again if the current increases, showing that the cathodic film now will begin to form. During this period as I think the cathode really will be quite free from any layer.

Dr. S. Wernick (*London*) said: With regard to the question of oxide occlusion in the deposit which resulted in grain-size reduction of nickel deposits, has any positive evidence been discovered by the various workers in the field of the presence of oxygen in a nickel deposit? I believe that the view that grain-size reduction in nickel was due to oxide formation and occlusion as a result of high p_H at the cathode was first put forward by O'Sullivan⁹ and has since been confirmed and accepted by subsequent workers in this field. O'Sullivan with whom I was in day-to-day contact at one time, made very careful attempts to discover oxygen in nickel deposits, but, so far as I am

⁸ T. Erdey-Grúz, *Z. physikal. Chem.*, 1935, **A172**, 157.

⁹ *Trans. Faraday Soc.*, 1930, **26**, 89.

aware, no positive results were obtained. Possibly other investigators present have been more fortunate.

Professor A. Glazunov (*Přibram*) said :

The inclusions in the cathodic deposit may be divided into two groups : 1. The inclusion is either a mechanical inclusion among the crystal grains of the cathodic metal deposit ; 2. Or it is a part of its space lattice.

The inclusions of the first group are remainders of the electrolyte among the branches of crystals, and (in case the p_H of the electrolyte is insufficient), oxides and hydroxides of the metal in question.

The quantity of these inclusions depends especially on external factors under which the electrolysis takes place, i.e., the concentration of the electrolyte, the current density and the temperature. The growth of the cathodic deposit, i.e., its crystallisation depends not only, as usual, on the kg_I and kz ¹⁰ but also on $kg_{II}(cv_{II})$, i.e. on, the crystallisation velocity perpendicular to the cv_I .¹¹ cv_I is the crystallisation velocity of crystal growth perpendicular to the surface of the cathode and cv_{II} parallel to it (Fig. 1).

All these crystallisation factors increase with increase of current density, but not to the same degree :

$$\frac{dcv_I}{di} \neq \frac{dcv_{II}}{di}.$$

As to the influence of the concentration, nc and cv_I decrease with the increase of the concentration, while cv_{II} increases.

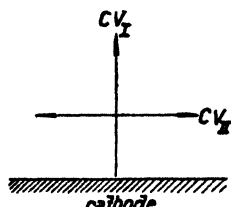


FIG. 1.

It is obvious that in case of a small cv_{II} the crystals will grow, but the space between individual dendrites will not at once be filled.

Further deposit will take place especially at the ends of crystals and between them there will remain gaps filled with the rest of the electrolyte (Fig. 2*).

In case of a small p_H the hydroxide produced will be deposited among the individual dendrite branches and in this way inclusions of hydroxide appear.

The composition of the electrolyte has the influence on cv_I , cv_{II} and nc (in case of complicated ions cv_I is small but cv_{II} as well as nc is greater) the possibility of inclusion production become smaller.

As to the inclusions of the second group I am of the same mind as Dr. Glasstone that they can appear only by discharge of complex cations of the type Ag_2CN^+ or Ag_2I^+ ; this seems to be confirmed by Professor Schlötter's experiments.

Dr. L. Tronstad (*Trondheim*) said : In discussing the questions put forward by Dr. Liebreich it is essential to distinguish between two

¹⁰ $kg_I = cv_I =$ crystallisation velocity, $kz = nc =$ number of crystallisation centres.

¹¹ A. Glazunov and O. Rada, *Relation entre la direction d'accroissement du dépôt cathodique et la forme des lignes des forces électriques*.—*Chimie et Industrie*, XII^e Congrès, 1932, Prague ; A. Glazunov and J. Janoušek, kz , kg_I et kg_{II} pendant la formation de dépôt cathodique.—*Chimie et Industrie*, XII^e Congrès, 1932, Prague ; A. Glazunov, *Über das Gefüge des kathodischen Niederschlags*, *Z. physik. Chemie*, 1934, 167, 399.

* Plate LVII.

different kinds of surface films, which can be present on a cathode (completely degreased). Firstly, there is the normal oxide film which is usually initially present on metals and is very difficult to remove in neutral or even slightly acid solution.¹² This is mainly due to the fact that the current density on the electrode is usually not homogeneous, *i.e.* the hydrogen evolution takes place mainly at active centres. Secondly, one has to deal with films formed on the working cathode by chemical reactions, etc.¹³ These films consist often of hydroxides and are usually more porous than the normal oxide films, and they can thus be more readily removed. It is well known, for instance, that the formation of such hydroxide layers on the cathode occurs during electrodeposition of nickel from aqueous solution, when the p_H rises above a certain critical limiting value.

Dr. C. Kasper (*Washington*) (*communicated*): I have recently succeeded in proving that in chromium deposition from the chromic acid bath, the deposition occurs directly from the sexivalent state. In fact, the evidence which is primarily based on the non-deposition of copper, nickel, and iron from the chromic acid bath, is so conclusive it is possible to assert that the particular dichromate ions which are reduced to the metallic state never exist in any form that may be identified with tri-valent or bi-valent chromium. The article containing the proof will appear shortly in the *National Bureau of Standards Journal of Research*.

This view is in direct antithesis with that presented by Dr. Liebreich. Furthermore, the very great polarisation which is encountered in that reaction may be quite adequately accounted for by the character of the rate-determining steps of the reaction involved. The effect of the basis metal to which Dr. Liebreich refers, is related to the hydrogen over-voltage of that metal.

It is not to be expected that hydriodic acid would be an effective addition agent, as the iodide ion cannot exist in conjunction with chromic acid. His observations on the cathodic solution of iron in chromic acid at low current densities are interesting, but I wish to point out that they are at variance with results that he reports for copper.

Dr. H. J. T. Ellingham (*London*) said: An investigation of the variation of cathode potential with time during electrolysis, at various constant current densities, of nickel sulphate solutions containing nickel hydroxide in suspension had been carried out in his laboratory by Mr. C. J. W. Hooper, and the results seemed to have some bearing on the question raised by several authors in this group of papers—the influence of hydroxides, oxides or other metallic compounds on the structure of electro-deposited metals. At the beginning of electrolysis, these high p_H nickel solutions yielded only a sooty black powdery deposit, accompanied by slight hydrogen evolution, and the polarisation was of comparable magnitude with that accompanying nickel deposition from the usual type of plating bath. After a certain time, however, the cathode potential generally underwent a sudden change to less negative values, not far removed from the reversible

¹² Compare L. Tronstad and T. Høverstad, *Z. physikal. Chem.*, 1934, **170A**, 172.

¹³ L. Tronstad, *Det Kgl. Norske Videnskabers Selskabs Forhandlinger*, 1931, **4**, 161; *Z. physikal. Chem.*, 1932, **A 158**, 369.

deposition potential of nickel: thereafter periodic variations of cathode potential took place, the polarisation oscillating between very small values, such as are not usually observed in nickel deposition, and very high values at which vigorous hydrogen evolution took place and green nickel hydroxide was deposited on the cathode. If electrolysis were interrupted some time after the sharp fall in polarisation, a film of bright nickel was often found on the cathode underlying the black powdery deposit or the layer of green hydroxide. From a consideration of the results of this work, it seems not improbable that bright nickel deposits may be formed only by way of some unstable intermediate product—possibly an oxide, or an unstable modification of the metal requiring a moderately high polarisation for its production. Under the conditions of these experiments the production of this intermediate system and its subsequent conversion to a bright metallic deposit appeared to take place during separate time intervals, and could thus be distinguished by the different ranges of cathode potential at which they occurred; whereas in deposition of nickel from the usual types of plating bath, the two stages might take place in very rapid succession. The high polarisation normally associated with nickel deposition and the fine grained structure of the metal produced even from simple salt solutions of suitable p_H value, might be due to some such mechanism.

Dr. C. Kasper (*Washington*) (*communicated*): The region of electrolytic reduction and the influence of films upon it, discussed in the paper, is somewhat outside the domain in which metallic chromium is deposited, but ideas and facts that have been developed in that domain may be of importance in elucidating the character of the reactions which are involved. The rather interesting situation is presented by the facts which Professor Müller presents, in that we can have a reaction occurring at the same rate at different potentials. Frankly, the type of theory that I have found necessary to account for action of the sulphate upon the film in the polarisation regions where metallic chromium is deposited cannot be said to hold here. However, there are several inconsistencies in the view Professor Müller submits.

First, the conception of the sol particles as regularly oriented molecules, appears as an extremely fortuitous status of affairs. Second, it has been established that the basic sol comprising the film exists at p_H of 3 or more; it is scarcely to be presumed that the bisulphate ion could be effective. Third, Müller's theory would specifically demand that the fluoride ion be much more effective than the sulphate. I would be interested to know whether Professor Müller had any data on the last point. It is well known, of course, that in the region of electrolytic reduction where metallic chromium is deposited, the inverse is true. I would further like to point out the extreme difficulty of accounting for *exactly* the same reaction in every detail, occurring at the same rate, at two widely different potentials. This point is the thesis of Müller's arguments. I would also like to know how Professor Müller accounts for the fact that chromic acid solutions can possess a maximum in the current efficiency/sulphate concentration curve.

H. Reininger (*Leipzig*) said: The papers by W. Blum, D. J. Macnaughtan and M. Schlötter, as well as the discussion remarks by A. W. Hotherhall, contain references to the "hardness" of different galvanic deposits. The actual numbers have been obtained mainly

by the use of the Brinell apparatus. I consider the results obtained by the method of Brinell—as well as by other usual methods, developed by Rockwell, Vickers, Shore (Scleroscope), Martens (scratch-hardness), etc.—to be of a very doubtful value, at least in the case in question. Conditions under which these results are really useful are not fulfilled in the case of galvanic deposits. Quite generally, the data which purport to characterise the “hardness” of different materials, correspond to no well-defined physical property. This is implied in the conventional definition of what is meant by “hardness,” viz. “the resistance offered by a material against the intrusion of a foreign body” (*e.g.*, of a Brinell-ball). Even in the simplest case—that of a mono-phasic structure (single crystals or polycrystalline aggregations of pure metals or homogeneous mixed crystals), with a homogeneous test-surface, the resistance actually measured is only a sum of single resistances against deformations of different kinds, which are permanently changing with growing deformation. Due to the well-known “hardening” effect of deformation on crystals (“cold hardening”), these resistances grow during the experiment, until the process of deformation is stopped at a point determined by the load and by the duration of the test. At this moment the state of the material is still more or less different from the state of the greatest possible hardening. The method thus gives numbers lying somewhere between the lowest initial and the highest ultimate resistance. Despite these vicissitudes, the data obtained in this way are practically useful and characteristic of the relative resistibility of different materials, as long as mono-phasic homogeneous bodies are concerned, and under the conditions in which they are being tested so long as such conditions are strictly invariable (same form and size of the thrusting body, invariable load and constant duration of the experiment). The practical uncertainty becomes really dangerous when the general difficulties are enhanced by the existence of rough inhomogeneities in the structure tested. The meaning of the hardness-numbers (somewhat doubtful even in the simplest cases) becomes highly uncertain if the surface is poly-phasic, each phase having its own deformation-resistance—*i.e.*, its own “hardness.” Possible local variations of the relative concentration of the components further diminish the possibility of obtaining data which are really characteristic of the “hardness” of the material as a whole.

In this way, even purely microscopical inhomogeneity of the structure enhances the uncertainty of the measurements. The situation becomes worse if the inhomogeneity of the material is such as to be visible to the naked eye. This is the case with all kind of metal coatings, as well as with surface-layers of metals made different from the “core” by special processes—*e.g.*, hardened surfaces of softer iron or steel. In all these cases it is extremely difficult to obtain data which really refer to the hardness of the coating in itself. Especially when thin coatings are concerned, it is nearly impossible to make the thrusting instrument so small as to prevent any deformation of the base underneath the coating. The “hardness” will therefore depend on the sum of the resistances offered by the coating *and* by the base-metal, and will never be a characteristic constant of the coating in itself. It is of course possible to prepare thicker coatings and to use small balls, pyramids or scratching instruments, in the hope of avoiding

any interaction between the instrument and the base-metal. Quite apart from the difficulty of ensuring such a limited action of the instrument, the use of specially prepared thick layers involves another great uncertainty, since the properties of such layers may be entirely different from those of the thin and thinnest coatings in which we are actually interested. The mechanical properties of the latter are strongly affected by surface-forces (surface-tensions, residual valencies) prevailing at the boundary between coating and base. This makes it dangerous to apply to thin coatings the "hardness-numbers" obtained with thick layers. The data quoted for the hardness of galvanic deposits thus become still less reliable.

Professor M. Schlötter told us that he was able to obtain reliable values for the "hardness" of galvanic deposits by the use of a "differential" method. He first measured the hardness of the material before coating, and then the hardness of the same sample after it had

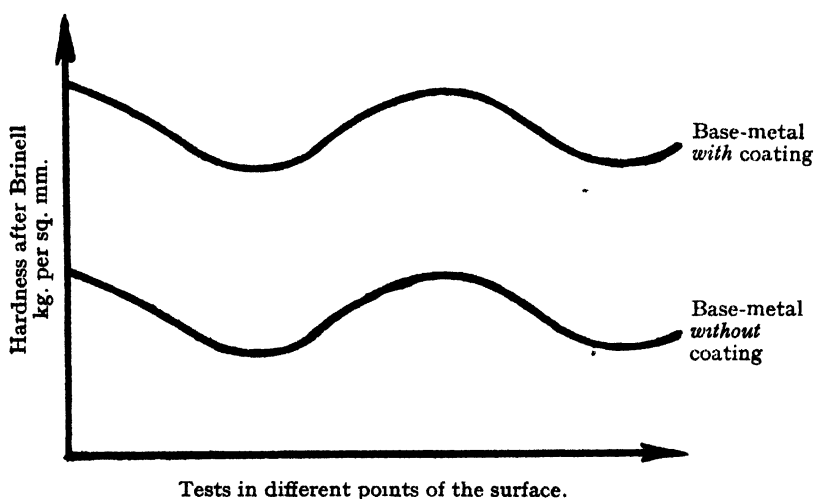


FIG. 3.

been covered with the galvanic deposit. Fig. 3 shows his results schematically. The curves represent the "hardness" (measured by the method of Brinell), as it changes from point to point on the surface of the material. The lower curve refers to the metal without coating, the upper to the coated material. The difference between the two curves is constant and is believed to represent the true hardness of the coating.

This method appears at first to be more reliable than all the others. But this is a superficial impression; the general criticism which was brought forward against the methods of measuring "hardness" in general, remain valid in this case too. The hardness which Schlötter finds in testing the coated material is dependent on the resistances of both the base and the coating (as I have pointed out in my previous remark). The problem of determining the "true" resistance of the coating itself remains unsolved. The simple method of calculation: "Hardness of the coating is equal to the hardness of the base subtracted

from the hardness of the coated material" leads to values which are different from those obtained by testing thick coatings of the same material.

Furthermore, the parallelism between the two curves in Fig. 3 can only be expected to hold in the case of an uniform base-metal (consisting either of a pure metal or of homogeneous mixed crystals, or of a very fine-grained eutectic mixture), with a constant resistance all over the surface. If the resistance varies from point to point, the parallelism of the curves may be completely destroyed. As an example we may quote soft ferritic cast-iron, which contains rough inclusions of graphite. My investigations¹⁴ showed that galvanic deposits adhere very badly to this material. As one can see from the section reproduced in Fig. 4,* the coating becomes loose and is easily split off on the places where the graphite appears on the surface of the base-metal. If we investigate the hardness of the piece shown in Fig. 4,* before coating, we obtain a curve of the type of the lower curve

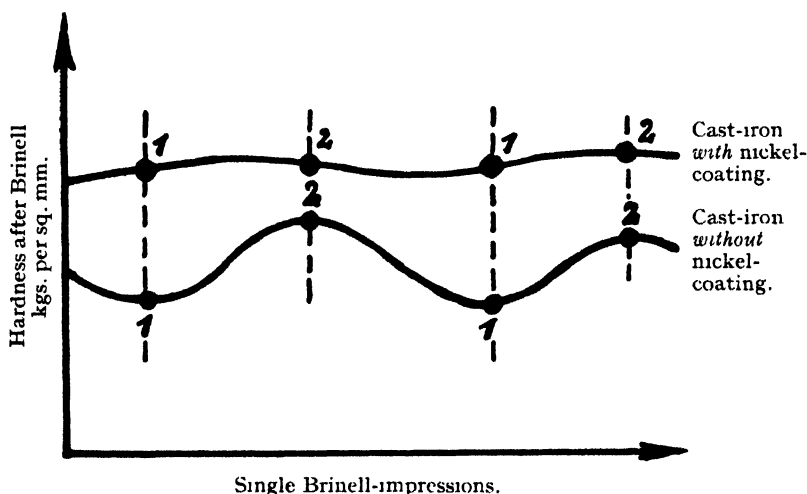


FIG. 5.

in Fig. 5. The low values (1) correspond to the points where the surface consists of graphite, the higher values (2) to the sections of the surface which are formed mainly by the ferritic substance. In measuring the hardness of the same material *after* coating, we may easily press pieces of the coating into the soft patches of graphite below. At these points we shall find the hardness strongly increased by coating; at the same time the hardness will be only very slightly changed at the points with a ferritic surface. We may thus get nearly a constant hardness all over the surface of the coated material, as shown by the upper curve in Fig. 5. It would be difficult to define the "hardness of the coating" as the difference between the two curves in a case like this.

¹⁴ *Z. Metallwaren-Industrie Galvanotechnik*, 1933, 31, 359, 379, 419.

* Plate LVII.

These remarks concerning the "differential" method of Professor Schlötter only enhance my general statement, that all methods of determination of the hardness of galvanic deposits are unexact, uncertain and unsuitable for precise characterisation of the mechanical properties of the materials in question.

My remarks lead to the conclusion that we may come nearer to the determination of the real resistance of the coatings by eliminating as far as possible any deformation of the base during the test. A possible way is to measure the relative hardness by comparing the forces which produce an impression of a given depth in the surfaces of different coatings (the depth being chosen as shallow as possible). We can, for instance, measure the depth h of the impression left by a 5 mm.-ball under the pressure P . If h is measured for different values of P , the diagram showing P as a function of h is found to be of the type given in Fig. 6. At small P -values the curve goes asymptotically over into a straight line OCG. At higher pressures, deviations from

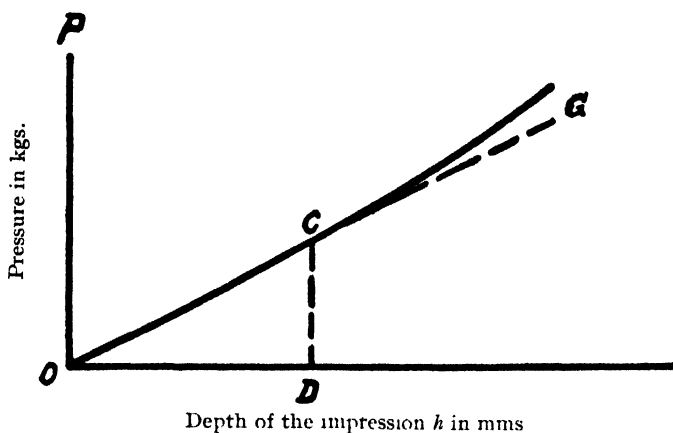


FIG. 6.

the straight line are observed, usually in the sense of h increasing "too slowly" with rising pressure, but sometimes in the opposite direction.

The proportionality between P and h makes it unnecessary to determine the function $P = f(h)$ over a great range; it is enough to measure P for a single value of h —a value as small as possible, and in any case smaller than OD in Fig. 6. We may, for instance, agree to consider $P_{0.05}$ as a measure of hardness—*i.e.*, the pressure which is necessary to press a 5 mm. ball 0.05 mm. deep into the coating.

Another point worth considering is the use of X-ray analysis in connection with the problems of structure, internal tensions and "hardness" of galvanic deposits. We refer to the phenomena of "asterism" as described by Fr. Rinne. He found that crystals which have been bent or otherwise deformed give disturbed Laue diagrams. Gross and Leonhardt calculated the shifting of the single Laue-points of deformed crystals, on the theory of gliding in crystals as developed by Mügge. The curves along which the points are shifted are approximately of the fourth order. A gliding in the direction R in a plane

E causes the lattice to turn about an axis lying in the plane E and perpendicular to R ("bending by gliding" mechanism). As a consequence, all planes in the lattice become cylindrical; in reflecting X-rays they behave as cylindrical mirrors, instead of plane mirrors, which they resembled before.

Analogous "asterical" phenomena are obtained with poly-crystalline materials. It is noteworthy that by using monochromatic X-rays—for instance the characteristic radiation of silver—only a part of the "asterical" pattern is obtained, in the form of radial stripes.

The occurrence of radial deformations of the regular diffraction-patterns offers a very sensitive method for the detection of inner tensions in the metals (tensions always meaning deformations of the lattice). W. A. Wood showed in his paper that such deformations actually occur in galvanic deposits. We may thus hope to find in the X-ray analysis a useful method for the investigation of the mechanic properties—as for instance inner strain or "hardness"—of galvanic coatings. It would be necessary to obtain sets of "asterical" Laue-diagrams (or some other equivalent diffraction-patterns) corresponding to different states of inner tension or to different hardnesses of the coating. We may hope to define these properties in this way more precisely than is now possible by means of the usual mechanical method of somewhat uncertain value.

Messrs. Macnaughtan and Hothersall (*London*), in reply (*communicated*):

Mr. Reininger states that the results of hardness tests of electrodeposited coatings are of doubtful value because of:—

1. Unreliability due to: (a) Influence of the basis metal and (b) Inhomogeneity of the deposit.
2. Inapplicability to thin coatings of the results obtained with thick deposits.

With respect to 1 (a), it has been made clear in the papers that deal with investigations on hardness by the Brinell and diamond pyramid tests that care was taken to eliminate the influence of the basis metal in a manner common to methods used in ordinary metallurgical technique in which this aspect has been fully explored (Moore, Hankins).

In respect to 1 (b), Mr. Reininger is evidently exaggerating the inhomogeneity of the deposit. With careful technique such as has been used in the Woolwich work the structure revealed by the microscope shows the deposit to be homogeneous and this is further emphasised by the fact that a consistent relationship has been found between hardness and tensile properties of the deposits, as in the case of forged carbon steels in which the relationship between the hardness and tensile test is put to extensive practical use.

With regard to 2, Mr. Reininger has not indicated the actual thickness of coating at which he regards the results obtained by us in our various communications as being inapplicable. In the vast majority of cases the thin coatings used in practice range in thickness from a few ten-thousandths to one or two ten-thousandths of an inch. In this range of thickness micro-examinations of cross-sections show that there is no marked divergence in the micro-structure of the bulk of the coating when compared with that of the thicker deposits necessarily employed for physical tests (hardness and tensile). It is possible, of course, that

with coatings of very much less thickness, which would seldom be used in practice, the influence of surface forces at the interface may affect the mechanical properties. In any study of the electrodeposition process, however, it is essential to diminish the influence of these surface forces, which in itself is a vindication of using thicker coatings, quite apart from the fact that they are the only means by which reliable quantitative results of physical properties can be obtained.

In reply to Dr. Wernick, we consider visual evidence of the presence of basic matter in electrodeposited nickel after annealing *in vacuo* as a positive indication of the presence of combined oxygen in the deposited metal. Analytical determinations, which are less reliable owing to the difficulty of determining small amounts of oxygen with accuracy, have shown a higher content of oxygen in hard than in soft deposits, thus confirming the results of visual examination. The suggestion that basic matter affects the structure of nickel deposits was made prior to O'Sullivan's work in 1930, notably by Oesterle.¹ Definite confirmation was first obtained in the work described in our paper.

Dr. E. Liebreich (*Berlin-Halensee*) said: It is quite true that the layer originating from the contact with the air must first be removed. This will be happening in the first part of the curve before the start of the reaction period. After this stage, a new layer is formed by the increase of the hydroxyl ions. The cathode will be clean just between both. This part of the curve is very small; the difficulty will consist in covering the whole cathode surface with the same current density. In solving this difficulty we always employed cathodes in the form of a point, using the end of a small wire. If this is not done the two other parts of the curve will be superposed.

Professor Müller, in reply, said: The assumption that the building-stones of the films are oriented molecules of chromium oxide—chromate is not so artificial as Dr. Kasper thinks. One must imagine the mechanism by which these films are formed on the flat surface of the cathode. Moreover, I see no other way of explaining many facts which have been discussed in my previous publications. I will mention only one.

A platinum sheet was polarised for some time in an aqueous solution of *purest* chromium acid, until hydrogen began to be evolved, but without reaching the potential at which chromium is deposited. After the current has been switched off, the potential of the cathode (which has been left in the acid for many hours) remained in the neighbourhood of the hydrogen potential. A long time was required before the potential returned to the value which is at once obtained when clean platinum is brought into contact with chromic acid. This shows that the cathodic film remains for a long time undissolved by chromic acid, which is strange, because chromic acid easily dissolves chromium hydroxide as well as chemically prepared chromium oxide-chromate. If one assumes that the molecules of the film are *oriented*, the stability of the film can be explained by the hypothesis that the acid has no access to the "vulnerable" parts of the molecules.

My theory is that an acid is driven into the pores of the film by electrolytic forces and can reach the basic groups of the molecules of the film and dissolve it, so long as its anions are not too large. HCrO_4^- ions are too large, but HSO_4^- ions are not. The mechanism, as I

¹ *Dissertation Tech. Hochschule, Zürich, 1928.*

imagine it, consists in H^+ -ions going in first, and HSO_4^- -ions following them; in this way, a H_2SO_4 -molecule is created in the film, and H_2SO_4 may of course be able to dissolve the material of the film.

Concerning the fluoride: A stronger action, as compared with sulphate, is shown by the fact that in its presence the reduction $Cr^{6+} \rightarrow Cr^{3+}$ proceeds at a lower potential than in the presence of sulphate.

Dr. Kasper finds it difficult to explain that the same reaction can take place, to the same extent, at two different potentials. This is actually observed in many cases. It would be enough to mention the fact that the electrolytic evolution of hydrogen takes place with a given current-density, at quite different potentials if cathodes with different "overvoltage" are used.

To proceed with a given velocity, each process requires a greater driving force, if the resistance is higher. In the case under discussion (*i.e.*, electrolytic reduction of Cr^{6+} to Cr^{3+}) a resistance is offered by the film on the surface of the cathode to the entering of a foreign anion into its pores. This resistance does not exist if, instead of a metal of the kind of platinum, the cathode is made of a material on which no surface films are formed—for instance carbon.

Dr. W. Blum (*Washington*), in reply, said: Undoubtedly the results obtained for either Brinell or scratch hardness on relatively thin coatings may be influenced by the hardness of the underlying metal. In the present experiments, however, the deposits were very thick (over 0.5 mm.), and were separated from the base metal. They were supported on a steel anvil during test. The surface was lightly polished so the results were not affected by any irregularities in the surface.

A few analyses at the National Bureau of Standards about ten years ago indicated the presence of small amounts of oxygen and hydrogen in apparently dense nickel deposits, but we have had no opportunity to confirm or extend these observations. On the other hand the suggested presence of included electrolyte in deposits must not be disregarded. It is at least probable that the reported presence of magnesium in nickel deposits, and of aluminium in zinc deposits, from baths containing these respective elements, was due to included electrolyte. Careful analyses of dense deposits made at the National Bureau of Standards failed to detect either of these elements.

ELECTRODE POTENTIALS AND THE FORM OF ELECTRODEPOSITED METALS.

BY SAMUEL GLASSTONE.

Received 5th February, 1935.

There is little doubt that the state of an electrodeposited surface is connected in some manner with the potential at which it is formed, but the exact nature of the relationship is obscure; the number of factors involved is probably greater than is generally realised, and reference to some of them will be made in the present paper. The problem divides itself into two main aspects: there is on the one hand the connection between the cathode potential, or more strictly the polarisation, *i.e.*, the difference between the actual deposition potential and the reversible value, and the fact that certain metals deposit in a coarsely crystalline form, whereas others are almost invariably micro-crystalline, and on the other hand the relationship between polarisation and the form of the same metal when deposited from solutions of different types.

Polarisation and Form of Deposit with Different Metals.

It has often been supposed that the surface of a deposit is smooth and polished and the crystals are small when there is considerable polarisation during deposition, but when there is little polarisation the deposit consists of relatively large crystals. This is certainly true as far as the electrolysis of lead and nickel salt solutions is concerned: the cathode potentials in the former case remain close to the reversible values during deposition and coarse deposits with dendritic growths are generally obtained, but with the latter metal there is a fundamental irreversibility leading to appreciable polarisation even at low current densities, and smooth micro-crystalline deposits are almost invariably obtained. The relationship breaks down, however, in connection with the electrolysis of argentocyanide solutions. Although many authors have considered that there is a definite polarisation at the cathode when such solutions are electrolysed,¹ this view is probably incorrect. It has been shown recently that the change of potential of a silver cathode in an argentocyanide solution is almost entirely due to concentration effects and there is very little inherent polarisation,² yet it is from such solutions that smooth deposits of silver, consisting of minute crystals, are readily obtained. It may also be noted that above 75° deposition of iron occurs almost reversibly from ferrous sulphate solutions,³ but the metal is in a smooth coherent form, consisting of small, apparently fibrous, crystals.⁴ These

¹ Cf. Aten and Boerlage, *Rec. trav. chim.*, 1920, **39**, 720.

² Glasstone, *J. Chem. Soc.*, 1929, 690.

³ *Idem*, *ibid.*, 1926, 2887.

⁴ Hughes, "Modern Electroplating," 1923, Chap. V.

observations cast doubt on the suggested relationship between polarisation and the type of deposit obtained, and it seems necessary to look elsewhere for an explanation of the facts.

Colloidal Material.

There are probably several factors of a gross nature operative in determining the size of electrodeposited crystals and these may or may not affect the potential in a definite manner. An obvious consideration is, of course, the possibility of colloidal material being present in the vicinity of the cathode, for if so it might have the effect, as colloids generally do, of diminishing the crystal size. Even in a relatively acid solution of an iron or a nickel salt the electrolyte will be relatively more alkaline in the immediate vicinity of the cathode than it is in the bulk of the electrolyte, owing to the fact that hydrogen ions are being discharged. There will thus be a possibility that the hydroxide of the metal will be precipitated, and this will certainly interfere with crystal growth; it appears quite definite that even smooth bright nickel deposits contain hydroxide of the metal, and this may well account for the micro-crystalline form.⁵ It is well known that colloidal materials tend to raise the cathode potential, but the amount of colloid present in a nickel deposit does not seem to be sufficient to account for the marked polarisation observed even at low current densities. It is not improbable, therefore, that the smoothness of a nickel deposit has little relationship to the fact that it is formed at a potential considerably removed from the reversible value. There may be some connection between the polarisation and the state of strain of the deposited nickel,⁶ since both diminish as the temperature is raised; it is not impossible, however, that the parallelism is quite fortuitous.

Electrolysis of Argentocyanide Solutions.

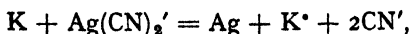
It has been already stated that there is no marked polarisation, apart from concentration effects, when silver is deposited from argentocyanide solutions and so it is necessary to find other factors to account for the finely-crystalline deposit. Kohlschütter has stated that even in argentocyanide solutions colloidal substances are present at the cathode,⁷ and that these account for the formation of the fine-grained deposits. The experimental evidence upon which this conclusion is based does not appear to be absolutely convincing, and it is as well to consider other possibilities. Some workers have suggested that minute crystals are formed because the silver-ion concentration in argentocyanide solutions is so low: it is true that when very dilute solutions are electrolysed the deposits consist of small crystals, but they are generally of a spongy form whereas those from the complex silver solution are smooth and coherent. If the rate of dissociation of argentocyanide ions into simple silver ions is a rapid process, and there seems good reason to believe that it is,² then there should never be any deficiency of silver ions in the double layer through which actual crystal growth occurs, and the low concentration of actual silver ions should be no handicap to the formation of large crystals. It is possible that the origin of the smooth deposits is to be

⁵ O'Sullivan, *Trans. Faraday Soc.*, 1930, **26**, 89; Macnaughtan and Hammond, *ibid.*, 1931, **27**, 633; Macnaughtan, Gardam and Hammond, *ibid.*, 1933, **29**, 729.

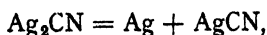
⁶ See Kohlschütter, *Trans. Amer. Electrochem. Soc.*, 1924, **45**, 229.

⁷ *Z. Elektrochem.*, 1913, **19**, 181.

found in the indirect discharge of silver ions. Since the concentration of these ions is as low as 10^{-20} g. ions per litre in argentocyanide solutions it has been suggested⁸ that the potassium ions are primarily discharged, and that the resulting potassium atoms react thus



to form silver. It is not unreasonable to suppose that under such conditions the crystals will have less opportunity to grow than if the simple ions were discharged directly as they are from silver nitrate solution. In view of the high negative deposition potential of potassium however, it does not seem probable that the ions will be discharged, and, the alternative view³ has been proposed that complex cations of the type Ag_2CN^{\bullet} , which appear to be present in argentocyanide solutions, are actually discharged at the cathode. The radicals formed will then decompose, for example as follows :



to form metallic silver, and under these conditions it is not difficult to, conceive the possibility of fresh crystal nucleus formation being favoured in preference to the growth of nuclei already present. Some of the silver cyanide formed simultaneously may even play a part in preventing crystal growth.

Deposition of the Same Metal under Different Conditions.

As far as the discussion hitherto has covered the subject of the deposition of the same metal from different solutions, the cases considered have been such that the electrolytes differed fundamentally, *e.g.*, silver nitrate and alkali argentocyanide, but there are many instances in which relatively small variations in the properties of the solutions bring about marked changes in the nature of the deposit. The most striking of these changes is that resulting from the addition of colloidal material to the electrolyte, when a solution which normally gives relatively large crystals on electrolysis, *e.g.*, lead acetate, may be made to yield a fine-grained deposit. It is true that the presence of colloidal material generally raises the cathode potential, but it is by no means certain that the formation of small crystals and the increased polarisation can be directly related to one another.⁹ The effect of the colloidal material in the formation of the deposit is probably purely topochemical in nature, since it acts by inhibiting the growth of the crystals, whereas the influence on the potential may be connected with the change in the cathodic environment. It appears essential, therefore, when attempting to establish a correlation between electrode potential and the nature of the deposit to rule out all cases in which topochemical factors of an obvious kind are operative. For this reason it is doubtful if the observations made during the deposition of nickel from solutions of its simple salts have any significance in connection with the present problem.¹⁰ It has been found that the hardness and stress in a nickel deposit have apparently no connection with the potential at which it is formed, but if the properties of

⁸ See, for example, Dean and Cheng, *Chem. Met. Eng.*, 1918, 19, 83; Hughes, *op. cit.*, p. 115.

⁹ See, however, Clark and Jones, *Trans. Faraday Soc.*, 1929, 25, 583, and discussion, *ibid.*, 1930, 26, 96.

¹⁰ Macnaughtan and Hotherhall, *ibid.*, 1928, 24, 387; Macnaughtan and Hammond, *loc. cit.*, 5.

the deposit are determined primarily by the included basic material, this result is not unexpected. Such observations, however, do not rule out the possibility of some fundamental connection, which may be obscured by other factors, between the potential and the type of crystal constituting the electro-deposit.

Direct Connections between Potential and Crystal Size.

A cursory examination of the subject reveals three ways in which cathode potential and size of crystal may be directly related when deposition occurs from a given electrolyte.

(a) If the change of potential with current density is large, the formation of small crystals will be favoured,¹¹ for as a consequence the effective area of the electrode is increased and the current density is decreased, so that any tendency of the cathode potential to rise will be opposed. The potentials which should be considered in this case are not strictly the measured values, since allowance should be made for concentration polarisation. Any deviation from the reversible value for which the latter is responsible is not likely to be influenced by a change in the effective area of the crystals; the concentration polarisation at a platinised platinum cathode, for example, is very little different from that at a smooth electrode of the same metal.

(b) It is a thermodynamic necessity that small crystals should be deposited at a more negative reversible potential than large crystals of the same metal, quite apart from polarisation effects which may be superimposed. This subject has been considered in some detail by Blum and Rawdon,¹² who apparently consider the factor to be an important one, but it is highly probable that although the difference in crystal size must have some influence on the deposition potential the actual effect is relatively small, being of the order of a few millivolts at most.¹³

(c) Both factors already considered imply that appreciable polarisation is associated with small crystals, but another aspect of the problem shows that the deposition of large crystals can involve greater polarisation than is the case with small ones. Volmer¹⁴ has shown that when zinc is deposited from zinc sulphate solutions there is very little polarisation if the cathode consists of small crystals of zinc, but it is quite appreciable when a surface made of large crystals is used. This difference is attributed to the retardation phenomena involved in the building up of the space lattice of the crystal; when the surface is made up of small crystals the newly-formed atoms will soon be accommodated, but when the lattices are large there may be a considerable delay, during which the discharged atoms remain in an intermediate state, and polarisation results.

Indirect Connections between Potential and Crystal Size.

Apart from the direct relationships between the potential and the form of the deposit, there are a number of indirect factors which must be considered. At very low current densities the rate of discharge of

¹¹ Aten and Boerlage, ref. 1; the variation of potential with *C.D.* probably affects the "throwing power" of the electrolytic bath, but this is a macroscopic factor outside the scope of the present paper.

¹² *Trans. Amer. Electrochem. Soc.*, 1923, 44, 397.

¹³ See Foerster and Deckert, *Z. Elektrochem.*, 1930, 36, 901; Hunt, *J. Physical Chem.*, 1932, 36, 1006.

¹⁴ *Z. physikal. Chem.*, 1928, 139, 597.

ions is small and so the rate of crystal growth may easily keep pace with the rate of liberation of metal atoms; under such conditions it is probably easier for crystals to grow than for fresh nuclei to be formed, and so the deposits are coarsely crystalline. At higher current densities, however, the rate of crystal growth may not be sufficient to cope with the atoms liberated and so fresh nuclei will be formed and a fine-grained or even spongy deposit is obtained. Increase of current density thus causes the size of the crystals to diminish. At the same time, but independently, increase of current density will be accompanied by an increase of polarisation, so that high cathodic potentials will be associated with small crystals, although the connection may only be indirect.

The effect of changing the electrolyte concentration is somewhat analogous to that of changing the current density, although the results are more complicated. It appears that decrease of concentration brings about an increase in the rate of growth of the crystals in a direction perpendicular to the cathode, but decreases the rate of growth over the surface;¹⁵ the polarisation, mainly due to impoverishment of the electrolyte, increases at the same time.

Alteration of temperature will also affect, to some extent, both the nature of the deposit and the potential independently. An increase of temperature tends to compensate for decrease of concentration and favours the formation of uniform, fine-grained deposits, but it may also accelerate the rate of crystal growth and so tend to yield large crystals. The cathodic polarisation decreases as the temperature is raised, and this may consequently, according to circumstances, be associated with either fine or coarse deposits.

Influence of Neutral Salts.

In conclusion, another factor able to influence both deposit and potential must be considered: this is the effect of the addition of apparently neutral electrolytes to the deposition bath, even when the formation of colloidal material is not probable. The observations made hitherto are, however, very complex and there appears little possibility of any direct correlation. For example, in the electrodeposition of silver from argentocyanide solutions the addition of various salts of alkali metals results in an increase of cathode potential, but the deposits obtained vary according to the nature of the anion added.¹⁶ Carbonate and nitrate give smooth uniform deposits, but with most other salts the surface of the silver is generally patchy in appearance and difficult to polish. In spite of the definite variations in the type of deposit obtained, no correlation with the cathode potential could be established. The addition of cyanate to an argentocyanide bath results in a definite decrease of potential, and at the same time the deposited silver becomes bright in appearance;¹⁷ the same brightening of the surface and a similar decrease of cathode potential is observed when carbon disulphide or alkali sulphides, in small amounts, are added to the argentocyanide solution.¹⁸ In these instances there must be a definite connection between the cathode potential and the nature of the deposit, the lower

¹⁵ Glazunov, *Z. physikal. Chem.*, 1934, **167**, 399.

¹⁶ Glasstone and Sanigar, *Trans. Faraday Soc.*, 1929, **25**, 590.

¹⁷ *Idem, ibid.*, 1931, **27**, 309.

¹⁸ *Idem, unpublished observations*; Haring, *Trans. Amer. Electrochem. Soc.*, 1926, **49**, 417.

potential corresponding with the formation of apparently smaller crystals. With the other alkali metal salts for which no such correlation could be found, it is probable that the cathode potential is affected by both cations and anions accumulating in the vicinity of the electrode, but that the anions alone affect the nature of the deposit, possibly by being adsorbed on the surface of the metal and so affecting crystal growth. Different potentials are observed in analogous sodium and potassium argentocyanide solutions, but the deposits obtained from them do not differ in any marked degree; hence alkali-metal cations do not appear to influence the development of the silver crystals. The added anions affect both potential and deposit independently, in the majority of cases; the exact nature of the respective influences is by no means clear, but it seems certain that as a general rule they are not related in any simple manner.

Conclusion.

It is evident from the analysis of the problem presented here that there must be some connection between the form of an electrodeposited metal and the electrode potential operative during its production, but owing to the fact that the influences sometimes work in opposite directions and to the number of complicating factors it is only rarely possible to determine the exact relationship. Before any set of observations is considered to support or oppose any particular view, it is essential to analyse the experimental conditions so as to ensure the absence of incidental factors which may obscure the fundamental connection between cathode potential and the nature of the deposit obtained.

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FACTORS AFFECTING THE STRUCTURE AND GRAIN SIZE OF ELECTRODEPOSITED CADMIUM.

BY S. WERNICK, PH.D., M.Sc.

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The electrodeposition of cadmium on ferrous metals as a corrosion-preventive has become so widespread that it represents the most important industrial application of this metal at present. Its efficacy as a rust-preventive is basically due to the fact that under ordinary conditions, cadmium, like zinc, acts anodically to iron and protects it by corroding "sacrificially" when the basis metal is exposed through abrasion, or other fortuitous circumstance.

The degree of protection which electrodeposited cadmium confers is dependent on a number of factors, *e.g.*, the type of electrolyte employed, conditions of electrolysis, nature of basis metal and so forth. The electrodeposit requires to possess a number of essential properties of which the most important are uniformity or even surface distribution, high degree of adhesion, freedom from pits, pores and inclusions of foreign matter and certain satisfactory physical properties such as freedom from internal stresses, reasonable hardness, non-brittleness and ductility. It has been found that the best type of deposit which is most likely to

embrace these properties is one possessing a compact and small-grained structure.

In the course of a number of studies connected with the electro-deposition of cadmium, the author investigated, *inter alia*, the effect of electrolyte composition and conditions of electrolysis on the grain size of cadmium deposited from cyanide and sulphate baths respectively; these types of bath being most commonly used in practice. The results of these investigations are given below.

I. Cyanide Electrolyte.

Previous Work—Russell and Woolrich¹ patented the first cadmium cyanide electrolyte in 1841; it consisted of a solution of cadmium carbonate which had been dissolved in a slight excess of potassium cyanide. Since then, numerous recommended electrolytes have been published, the "free" cyanide contents of which have been considerably higher. Thus, Fischer² used an excess of "free" cyanide amounting to 30-35 per cent. There does not appear to have been any special reason for this wide diversity. Similarly, specified concentrations of metal in the electrolyte have ranged from less than 10 gm./litre to as much as 50-60 gm./litre,^{3,4,5,6,7,8} indicating no general agreement regarding optimum composition. As to conditions of deposition, the current densities specified have varied from 5 to 30 amps./ft.², while the specified temperature of electrolyte has ranged from room temperature to 60°-80° C.⁹—again indicating marked absence of unanimity.

Effect of Composition of Electrolyte on Grain Size of Electrodeposited Cadmium.

The effect of variation in metal, "free" cyanide and alkali content which are the essential and most common components of a cadmium cyanide electrolyte on the grain size of the deposit were determined by the author in the following manner.

The electrolyte was prepared by dissolving cadmium carbonate in potassium cyanide, while the alkali employed was caustic soda. The solution was placed in a small glass cell, the internal dimensions of which were 9.5 cm. × 4.5 cm. × 4.1 cm. The anodes consisted of refined cadmium, 6 cm. × 4.4 cm., and the cathodes of cold rolled, close-annealed, mild steel of similar dimensions. The current density was standardised at 10 amps./ft.² and the temperature of the electrolyte kept at 20° C., the solution being unagitated.

(1) **Effect of Cadmium Content**.—The cadmium content was varied from 8 to 40 gm./litre, the amount of free cyanide being negligible and no alkali addition being made for this series of experiments.

The microstructure of the deposit, which was examined under low magnification, could be clearly distinguished. That produced at the lowest metal content was greyish-white in colour, rather dark and relatively coarse-grained. A number of deposits obtained under the same conditions showed a tendency to pitting, particularly at the edges where the current density is high. The deposit was occasionally also "treed." With in-

¹ Russell and Woolrich, 1849, *ref. Pat. Invention*, 1850.

² Fischer, *Chem. Ztg.*, 1904, **28**, 1209.

³ Dylite Process Co., U.S.P. 1,537,047 (1924).

⁴ *Ibid.*, B.P. 178,422 (1922).

⁵ Graselli Chem. Co., U.S.P. 1,564,414 (1924).

⁶ *Ibid.*, D.R.P. 474,211 (1925).

⁷ Dylite Process Co., U.S.P. 1,536,858 (1922).

⁸ *Ibid.*, D.R.P. 379,365 (1922).

⁹ Mitt. Teichsverb., *Automobilind.*, 1928, 258.

creased cadmium content, the electrolyte produced deposits showing a progressive refinement, that obtained at the highest metal content examined (30-40 gm./litre) being much more finely crystalline in appearance. During this series of "runs," the anode was observed to darken, tending to foul, but this may be ascribed to deficiency in "free" cyanide in the solution. At the same time, the conductivity of the electrolyte improved progressively.

(ii) **Effect of "Free" Cyanide Content.**—The "free" cyanide addition to a standard electrolyte with a metal content of 30 gm./litre, was varied over a range of 25-150 per cent. (equivalent to 17-102 gm./litre of potassium cyanide). The effect of progressive addition of cyanide was even more marked than with increase in metal concentration. Whereas, even with high metal content (at low "free" cyanide) the deposit, even when fairly close-grained, is non-uniform, showing vertical streaks and also nodules on occasion, this defect disappears in the presence of adequate cyanide. From about 50 per cent. "free" cyanide content onwards, the deposit shows marked improvement in colour, approaching whiteness. The macro-structure, between 100-150 per cent. "free" cyanide, is compact and non-crystalline to the eye, and very finely grained when magnified. The increased cathodic gasing which occurs when very high concentration of cyanide is present makes it desirable, however, to limit the "free" cyanide content to 100 per cent.

(iii) **Effect of Caustic Soda.**—This constituent of a cadmium cyanide electrolyte is not as essential as the first two, but apart from beneficial effects in other directions (*e.g.*, increased conductance and restraining influence on anode dissolution), its presence in quantities in excess of 0.85 per cent. was found to aid materially the formation of a small-grained deposit, while it was also found to be an important factor in maintaining the colour and uniformity of the deposit. Examined over a concentration ranging from 0.15 to 1.5 per cent., the best results were obtained in the higher concentrations. 1.2-1.5 per cent. produced particularly excellent deposits and it is probable that even higher concentrations than the latter would have proved equally as valuable.

The precise cause of the beneficial effect of relatively high caustic concentration cannot be readily explained. One would expect that higher cadmium and "free" cyanide contents would aid the production of small-grain deposits, since these both tend to result in conditions which are known to favour grain-size reduction—a plentiful supply of the complex salt of cadmium, the ionisation of which is restrained. The caustic soda present does not appear to affect the ionisation to any degree, since, unlike zinc, it forms no salt equivalent to the zincate. It is probable, therefore, that its beneficial action results through its effect in maintaining an optimum p_H in the neighbourhood of the cathode.

Effects other than those due to Composition.

(iv) **Effect of Current Density.**—It is well-known that current density has a marked effect on structure, and this proved to be the case with an electrolyte containing 30 gm./litre of cadmium, 100 per cent. "free" cyanide and 1.5 per cent. caustic soda. Examined over a range 10-50 amps./ft.², the deposit, which was initially white and finely-grained, became progressively greyer and more "crystalline." "Burnt" deposits were obtained at 30 amps./ft.² and at 40 amps./ft.², a dark, nodular and large-grained deposit was formed. By stirring the electrolyte, a deposit of fair quality could, however, be produced even at a high current density (as high as 50 amps./ft.²).

(v) **Effect of Solution Temperature.**—Using the solution mentioned under (iv), the effect of increasing the temperature from 20° C. to 70° C. was determined. Marked deterioration in the physical properties of the deposit occurred at temperatures in excess of 30-35° C. Very thin deposits (of the order 4×10^{-6} to 1×10^{-6} cm.) were relatively small-grained,

but when built up to the thickness usually formed throughout this work, i.e., of the order 2×10^{-4} , they became visibly crystalline or loose and spongy, resulting in fact in the worst quality deposits so far produced in the higher temperature range.

II. Electrodeposition from Cadmium Sulphate Solutions.

Unlike copper, nickel and zinc, cadmium when electrodeposited from a solution of its sulphate is produced in a highly crystalline state. It is possible, however, to modify its structure very considerably by various additions to the electrolyte and also by altering the conditions of electrolysis. The production of unsatisfactory deposits, both spongy and "treed," was recorded by Holtz.¹⁰ Desch and Vellan¹¹ made a study of the sulphate electrolyte among a number of others, their object being mainly to obtain a satisfactory cadmium deposit on aluminium and its alloys; it is interesting to note that their best results were obtained from a solution containing ammonium sulphate with peptone as an "addition" agent. Other addition agents employed were gelatin by Millian¹² and glue and caramelised sugar by Humphries.^{13, 14}

Similar apparatus to that already described was used for this series of experiments, the cathode again being cold-rolled, close-annealed mild steel. Cadmium sulphate of molar concentration was employed and all chemicals used were of A.R. quality.

Effect of p_H .—It was early evident that consecutive "runs" resulted in deposits which varied despite the maintenance of strictly similar conditions and, on investigation, the p_H of the solution was found to be rising comparatively rapidly. This variation in p_H had a marked effect on the crystal size of the deposit, which varied from large crystals at a p_H of 3.6 to quite small ones at p_H 5.3 and upwards (see Figs. 4 to 7).^{*} Accordingly, a number of additions of buffer substances was made successively to the molar cadmium sulphate solution with a view to producing a well-buffered electrolyte within a p_H range favourable to the production of deposits of relatively small crystal size. This work¹⁵ resulted in the standardisation of the following solution: cadmium sulphate, molar; boric acid, 30 gm./litre; sodium chloride, deci-normal. Thereafter, the p_H range 5.5-6.6 was found to be productive of small-grained, but nevertheless definitely crystalline deposits, which were not comparable in refinement with those obtainable from cyanide electrolytes.

(i) **Effect of Current Density.**—The variation in current density from 10 to 85 amps./ft.² in the unstirred electrolyte was productive of quite notable improvement in the deposit. Both the adhesion and the colour of the deposit improved, the former quality to such an extent that the deposit became burnishable when the current density exceeded 35 amps./ft.². If the electrolyte was agitated, still further crystal-size reduction occurred. "Treeing" of the deposit, however, took place when the current density exceeded 45 amps./ft.², even when agitation was employed.

(ii) **Effect of Temperature.**—The effect on the structure of elevation in temperature above atmospheric was found to be most interesting. The temperature range explored was 22°C. to 80°C. A reduction in crystal size took place up to a temperature of 50°C., with simultaneous darkening of the deposit. Thereafter, the deposit became whiter but more crystalline. This somewhat unexpected result compares interestingly with those obtained when the temperature of the cyanide electrolyte is varied.

(iii) **Effect of Colloids.**—It became evident from the foregoing that no

¹⁰ Holtz, *Physikal. Z.*, 1905, 6, 483.

¹¹ Desch and Vellan, *Trans. Far. Soc.*, 1925, 21, 17.

¹² Millian, *Bull. Soc. Chim. Belg.*, 1923, 32, 143.

¹³ Humphries, B.P. 304,668 (1929).

¹⁴ *Ibid.*, 309,071 (1930).

¹⁵ Wernick, *Trans. Electrochem. Soc.*, 1932, 62, 75.

* Plates LVIII. to LX.

really effective, small-grained cadmium deposit could be produced from the sulphate solution without the aid of some means of refinement other than that which is obtainable by modifying the composition of the solution or the operating conditions. The effect of three * typical colloidal addition agents, namely, gelatin, dextrin and peptone, was therefore studied.

The standardised conditions were as follows: buffered electrolyte as already described; current density, 10 amps./ft.²; temperature, 18° C.; time of deposition, 15 minutes. The colloids were prepared by simple solution in distilled water, moderate heat being applied (by means of a water-bath) to effect this if necessary. The concentration in each case was 2 per cent., so that an addition of 1 c.c. to a bath containing 100 c.c. of the electrolyte increased the colloid content by 0.02 per cent. In the case of peptone, owing to its somewhat rapid tendency to putrefy, a very small amount of thymol was added for preservation purposes.

Even relatively very small concentrations of added colloid, *e.g.*, as little as 0.005 per cent. (equivalent to 50 parts per million) in the case of dextrin, were found to decrease the grain size of the deposit quite appreciably, resulting in visible improvement. The table indicates the nature and extent of the change effected by each colloid.

Concn. of Colloid Per Cent.	Appearance.
Addition agent: Dextrin.	
0.01	Relatively crystalline deposit; dark grey.
0.02	Uniform small white crystals.
0.04	Very small white crystals.
0.08	Dark grey, relatively "structureless" and matt deposit.
0.24	Dark grey, "structureless," matt deposit.
Addition agent: Peptone.	
0.02	Irregular, fine crystals; dark.
0.04	Dark grey, regular, fine crystals.
0.10	Dark, matt, almost "structureless" deposit.
0.20	Dark, matt, almost "structureless" deposit.
Addition agent: Gelatin.	
0.02	Very small, white crystals; general non-uniform, "patchy" appearance.
0.04	White, fine grained structure.
0.08	Almost "structureless" matt, white deposit.
0.16	Matt, white, "structureless" deposit.
Excess	Similar to above but showing dark circular "network" structure.

Grain size reduction does not necessarily also imply a more attractive appearance, being accompanied occasionally by a definite darkening of the deposit. Dextrin-containing solutions produce a dark grey deposit, while this effect is even more accentuated in the case of peptone, relatively small concentrations of which nevertheless readily reduce the crystal size. The whitest and most matt type of deposit was obtained from electrolytes containing gelatin as addition agent; these deposits were similar in appearance to those obtainable from cyanide solutions. Best results using gelatin were obtained when the concentration of the colloid was not less than 0.10 per cent. and not more than 0.20 per cent. When the concentration exceeded the latter figure appreciably a non-uniform type of

* Other colloids which were originally included in this study were abandoned as unsuitable for various practical reasons, *e.g.*, casein cannot be added to CdSO₄ solutions without causing precipitation.

deposit with peculiar circular dark patches made its appearance. A restrictive "optimum" range of this kind does not, however, appear to apply either to dextrin or peptone—at any rate within the concentrations examined. In either case, there is no point in exceeding a concentration of 0.25 per cent. of colloid as a maximum, the desirable concentration being somewhat less than this figure.

In conclusion, it is perhaps pertinent to add that in the course of some further work, somewhat outside the scope of this paper, concerned with the corrosion-resistance of cadmium deposits obtained by using the colloids mentioned, the order of effectiveness of the addition agents in aiding corrosion resistance proved to be peptone, gelatin and dextrin respectively. Corrosion resistance may be taken to run parallel with grain size reduction and the order mentioned is particularly interesting in that it falls into line with the "protective" theory of precipitation of colloids.¹⁸

¹⁸ Wernick, *Trans. Far. Soc.*, 1928, 24, 361.

INFLUENCE OF THE BASIS METAL ON THE STRUCTURE OF ELECTRODEPOSITS.*

By A. W. HOTHERSALL.

Received 19th February, 1935.

The normal microstructure of a coarsely crystalline electrodeposit formed on a very finely crystalline or neutral base, consists of columnar grains oriented at right angles to the surface of the basis metal. Near the starting face, the grains are narrow, terminating in points; as the distance from the starting face increases, it can be seen that certain less favourably placed grains are crowded out by the lateral growth of other grains and the structure becomes coarser.

Huntington¹ first noticed that the microstructure of a copper deposit could be influenced by that of the copper upon which it was deposited. Later, Blum and Rawdon² and Graham³ made a detailed study of the subject and showed that the microstructure of cast or annealed copper could be continued by a copper deposit prepared under conditions which favoured the formation of a coarsely crystalline deposit. Blum and Rawdon noticed that the orientation of the copper base, as indicated by etching figures, was copied by the deposit.

The microstructure of the basis metal is here defined as being continued when the microstructure of the deposit is seen to differ from the normal in two respects: (i) Instead of numerous columnar grains terminating in points at the starting face, relatively few grains are seen, and all, or nearly all, of these have broad bases; this implies that the first layers of atoms deposited build up the crystal lattice of the basis metal in preference to forming a random arrangement to constitute the nuclei of a new structure. (ii) The grain boundaries of the deposit and basis metal coincide.

Recent investigations have tended to show that the structure of electrodeposited metals is largely determined by the degree to which continued growth of crystals is hindered by the inclusion of foreign

* Communication from the Research Department, Woolwich.

¹ *Trans. Faraday Soc.*, 1905, 1, 324.

² *Trans. Amer. Electrochem. Soc.*, 1923, 44, 305.

³ *Ibid.*, 1923, 44, 427.

matter. A major source of interference in nickel deposition has been shown to be colloidal hydroxide.⁴ Hunt⁵ has suggested that other possible forms of interference are due to distortion of the growing lattice of the deposit by the inclusion of foreign ions, atoms or molecules; for example, the co-deposition of an element such as hydrogen to form a solid solution might so distort the lattice as to encourage the commencement of a new crystal growth with consequent grain refinement and change in orientation. In order to be able to assess the importance of this type of interference, it is necessary to know the magnitude of lattice distortion which is permissible without causing interference with crystal growth. The extent to which a new phase of different lattice dimensions or crystal form may promote the formation of new crystal growth in preference to continuation of existing grains may also be important, particularly in connection with the adhesion of deposits to an alloy in which more than one phase is present.

In this paper, examples are shown of attempts to secure continuation of the microstructure of several metals and alloys which differ from the deposit in crystal form, or in lattice constant, or in which the lattice has been distorted.

In a study by X-ray analysis, Wood⁶ has shown that the orientation of the basis metal may be copied by the deposit. Wood, however, was only able to detect similarity of orientation over a limited range of depositing conditions, and it appears likely that if there is much interference with crystal growth of the deposit, the normal structure and orientation of the deposit will be assumed within a short time from the commencement of deposition. It is obvious that if conditions of deposition are such as to cause the grain size of the deposit to be small, that is, if the continued growth of individual crystals is hindered so that no one crystal grows for an extended period, continuation of the grains of the basis metal may be confined to such a minute thickness of deposit as not to be visible in the microstructure. Any study by microscopic methods of the influence of the basis metal on the structure of the deposit must necessarily, therefore, be confined to those deposits which can be produced, by suitable control, with a fairly coarsely crystalline structure. Copper, deposited from the acid sulphate solution, is clearly one of the most suitable deposits, and has been chiefly used in this investigation. Some experiments have also been made with tin, deposited from the hot sodium stannate solution, and with nickel.

The primary object of this paper is to show the possibilities of using this method of study to throw further light on the structure and adhesion of electrodeposits.

It should be emphasised that positive evidence of continuation has been taken as the only valid criterion; absence of continuation may merely indicate that the technique used is insufficiently refined, and, unless confirmed in other ways, it should only be accepted with reserve.

Materials and Methods.

In addition to the necessity of using a deposit of fairly large grain size, the basis metal must be chemically clean and free from films of foreign matter; and it must not react chemically with the depositing solution to give a film which will prevent intimate contact of the deposit.

⁴ D. J. Macnaughtan, G. E. Gardam and R. A. F. Hammond, *Trans. Faraday Soc.*, 1933, **29**, 729.

⁵ *J. Physic. Chem.*, 1932, **36**, 2259.

⁶ *Proc. Physic. Soc.*, 1931, **43**, 138.

The selection of suitable cleaning procedures was made on the basis of experience in securing a high degree of adhesion. The cleaning procedures used comprised (a) removal of grease by the usual methods (organic solvents followed by immersion in a hot alkaline cleaning solution); (b) an etching treatment which varied according to the basis metal. Copper, copper-zinc alloys and silver were etched in nitric acid solution (50 : 50). Tin was anodically etched in sodium hydroxide solution. Iron was passivated anodically in sulphuric acid solution.

Since the intention in the present study was to vary the structure of the basis metal only, conditions of deposition were chosen which were known to give coarse-grained deposits, and they were kept constant. These conditions are shown in Table I.; their suitability was confirmed, but only partially for nickel, by the result that the microstructure of the cast or annealed metal was continued by a deposit of the same metal. Purified materials were used.

TABLE I.—CONDITIONS OF DEPOSITION.

Metal.	Solution, g. per litre.	Temp. °C.	Current Density, mps./dm ² .	ϕ_H Quinhydrone Electrode.
Copper .	CuSO ₄ 5H ₂ O — 250 H ₂ SO ₄ — 50	35	0.5	—
Nickel .	NiSO ₄ 7H ₂ O — 240 NiCl ₂ 6H ₂ O — 30 H ₃ BO ₃ — 30	45	1.0	3.5
Tin .	Sn — 80 (as Na ₂ SnO ₃) NaOH (free) — 20	75	1.5	—

The following basis metals were used: Copper (cast, also rolled and annealed); copper-zinc alloys (cast) containing 2, 10, 30, 40 and 46 per cent. Zn; nickel (rolled and annealed); iron (electrolytic, doubly refined, annealed in hydrogen at 950° C.); tin (cast); tin-antimony alloy (1 per cent. Sb, cast); silver (rolled and annealed).

Micro-Examination.

Deposition was in general continued for sufficient time to give a thickness of deposit greater than 0.5 mm. To maintain the level of the edge of the specimen during polishing a further thickness of deposit was applied at a more rapid rate, or the specimen was mounted in bakelite or in Wood's metal (from which it was removed prior to etching).

Difficulties were encountered in etching specimens of metals coated with a dissimilar deposit. Copper-plated brass specimens were etched by rubbing on Selvyt cloth moistened with a dilute ammoniacal solution of ammonium persulphate. Copper-plated silver was etched first in chromic acid solution (25 per cent. CrO₃) to develop the structure of the silver, and then in ammoniacal ammonium persulphate solution. Copper-plated nickel could only be etched satisfactorily by protecting the copper by means of cellulose varnish, whilst the nickel was etched in a mixture of nitric and acetic acids; the varnish was then removed and the copper etched in ammoniacal ammonium persulphate. Alternatively, the copper could be etched first and photographed and the nickel treated similarly, the two prints being matched.

Results.

(1) Deposits of Copper (face centred cube, 3.607 \AA^*).

With all specimens examined clear evidence of continuation of microstructure was obtained. The results, including the Fig. numbers which relate to them, are summarised in Table II.

TABLE II.—METALS, THE MICROSTRUCTURE OF WHICH WAS CONTINUED BY AN ELECTRODEPOSIT OF COPPER.

Basis Metal.	Condition.	Crystal System.	Lattice Constant, \AA .	Difference from Lattice Constant of Copper (3.607) Per Cent.	Micro-Structure shown in Fig. No.
Copper	Cold rolled, 30 per cent. reduction.	Face-centred cube	—	Distortion equivalent to 0.3 per cent. ⁷	1 †
Nickel	Annealed	Face-centred cube	3.52	— 2.4	2 †
Silver	Annealed	Face-centred cube	4.06	+ 12.5	3 †
Copper-Zinc alloys:					
98 : 2	Cast	α solid solution—face-centred cube	—	—	4 †
90 : 10	Cast		3.629 ⁸	+ 0.6	5 †
70 : 30	Cast		3.673 ⁸	+ 1.8	6 †
60 : 40	Cast	$\alpha + \beta$	α 3.693 ⁸	+ 2.4	7 †
54 : 46	Cast	β solid solution—body-centred cube.	2.94 ⁸	—	8 †

The microstructures of these copper deposits were characterised by being composed of exceptionally large grains, the boundaries of which coincided with grain boundaries in the basis metal. In the deposits on the copper-zinc alloys 60 : 40 and 54 : 46, a further structure was faintly visible within the large grains of the deposit.

(2) Deposits of Nickel (face-centred cube, 3.52 \AA).

Examples of continuation of a number of grains in the microstructure of rolled and annealed nickel (Fig. 9) † and of electrodeposited nickel which had been filed smooth (Fig. 10) † were obtained.

Deposits of nickel on iron (body-centred cube 2.86 \AA) showed evidence of some relationship between the microstructure of the two metals (Fig. 11). † In some sections, the orientation of the grains of the deposit appeared to vary slightly on different ferrite grains.

(3) Deposits of Tin (tetragonal, $a = 5.824 \text{ \AA}$, $c = 3.165 \text{ \AA}$).

Continuation of microstructure was obtained with deposits of tin on cast tin (Fig. 12), † and on cast tin-antimony alloy (99 : 1).

* The crystal system and lattice constant given here and later refer to the metal as produced by metallurgical methods.

⁷ W. A. Wood, *Phil. Mag.*, 1932, 14, 656.

⁸ Owen and Pickup, *Proc. Roy. Soc.*, 1932, 137, 397.

† Plates LXI-LXIV.

Evidence of continuation of microstructure was also obtained with deposits of tin on copper (Fig. 13).^{*} Owing to difficulties in polishing, due to the difference in hardness of tin and copper, it has not so far been possible to secure sharp definition of structure in both tin and copper simultaneously. There appeared, however, to be numerous examples of correspondence of grains in copper and tin.

The results for deposits of nickel and tin are summarised in Table III.

TABLE III.—SUMMARY OF RESULTS WITH ELECTRODEPOSITS OF NICKEL AND OF TIN.

Basis Metal.	Crystal System and Lattice Constant.	Deposit.	Crystal System and Lattice Constant (of Metal as Produced Metallurgically).	Microstructure.
Nickel, annealed	Face-centred cube, 3.52 Å.	Nickel	Face-centred cube, 3.52 Å	Numerous examples of continuation (see Fig. 9).
Nickel, electrodeposited and filed	Face-centred cube, 3.52 Å.	Nickel	Face-centred cube, 3.52 Å.	Numerous examples of continuation (see Fig. 10).
Iron, annealed	Body-centred cube, 2.86 Å.	Nickel	Face-centred cube, 3.52 Å.	Evidence of relationship (see Fig. 11).
Tin, cast	Tetragonal: $a = 5.824$ Å. $c = 3.165$ Å.	Tin	Tetragonal	Complete continuation (see Fig. 12).
Tin-antimony alloy 99 : 1, cast	—	Tin	Tetragonal	Numerous examples of continuation.
Copper annealed	Face-centred cube, 3.607 Å.	Tin	Tetragonal	Suggestion of complete continuation (see Fig. 13).

(4) **Macrostructure.**—In all specimens examined, the macrostructure of the deposit was clearly a reproduction of that of the basis metal. Where the microstructure was continued, the macrostructure of the basis metal was frequently emphasised by the deposit, becoming more pronounced with increasing thickness. Where the microstructure was not continued (as with nickel deposits on iron), the macrostructure of the basis metal became less clearly visible as the thickness of the deposit increased. Fig. 14^{*} shows the surface appearance of annealed electrolytic iron coated with a nickel deposit 0.05 mm. in thickness: with a thickness of 0.8 mm. the macrostructure of the iron was only faintly discernible. Fig. 14 shows that a deceptive impression may be obtained by attempting to judge the microstructure of an electrodeposited coating by examination of its surface appearance, since it would appear that the microstructure of the iron had been continued by the deposit, whereas actually the deposit had a normal fibrous structure.

^{*} Plate LXV.

Discussion of Results.

The results clearly show that continuation of a basis metal structure is possible, (a) when deposit and basis metal belong to the same crystal system, over a range of differences in lattice parameters (*e.g.*, from -2.4 to $+12.5$ per cent. difference), (b) when deposit and basis metal belong to different systems. Thus, tin (tetragonal) has been shown to continue the microstructure of copper (face-centred cube) and copper to continue that of β brass (body-centred cube). Confirmation of this result with other combinations of deposit and basis metal has not yet been obtained although a definite relationship between the microstructure of a nickel deposit and an iron base (body-centred cube) was observed. Electrodeposited nickel has, however, not been found specially suitable for use in this work, since there is sufficient interference with crystal growth to prevent the production of a coarse-grained deposit, even with the optimum conditions at present available.

Continuation of microstructure was not restricted when the lattice of the basis metal had been distorted either by the introduction of an element in solid solution (zinc in copper, maximum lattice distortion for α solid solution 2.4 per cent. according to Owen and Pickup⁸), or by cold deformation. Wood⁷ has shown that maximum lattice distortion on cold deformation of copper is secured with 25 per cent. reduction in thickness; perfect continuation of microstructure of copper, which had been reduced in thickness after annealing by 30 per cent. by cold rolling, was obtained with an electrodeposit of copper.

Thus it would appear that a considerable amount of distortion or change in the growing lattice of the deposit by the inclusion in solid solution, or combination, of foreign elements should be possible without marked interference with crystal growth. This throws doubt on the likelihood of any appreciable modification in grain size resulting from the co-deposition in solid solution of hydrogen, since the maximum increase in lattice parameter of palladium, which is exceptional in its ability to absorb hydrogen, is only 4.2 per cent. (with 47 atomic per cent. hydrogen) according to Krüger and Gehm.⁹

It also appears probable that the high degree of adhesion, obtainable with electrodeposited coatings, is associated with their ability, in some cases at least, to continue the crystal lattice of the metal upon which they are deposited, if only over a limited thickness.

To what extent continuation of structure is generally possible, and how it may be affected by differences in crystal form, lattice dimensions and orientation requires further investigation. The method used appears to have important possibilities and to be capable of extension to throw further light on the structure and adhesion of electrodeposited metals.

The author is indebted to his colleagues Mr. R. A. F. Hammond, for assistance in the experimental work, and Mr. H. Wrighton, for preparation of the photomicrographs.

⁹ *Ann. Physik.*, 1933, 16, 174.

DIFFERENCES IN THE STRUCTURE OF ELECTRODEPOSITED METALLIC COATINGS SHOWN BY X-RAY DIFFRACTION.

By W. A. Wood.

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The X-ray diffraction spectrum of an electrodeposited metallic coating is usually different from that of the metal in a normal annealed state. At the same time such physical properties as the hardness differ. This contribution discusses the modifications in structure indicated by the X-ray spectra, and the extent to which they may be associated with the physical properties of the coatings. Particular reference is made to nickel and chromium deposits. Similar differences characterise also the X-ray spectrum of a metal which has been strain-hardened by deformation; use will therefore be made of results obtained in this field. We consider first results on the grain size.

1. Grain Size.

By inspection of the spectrum the grain size can be assigned immediately to one of three classes: the first is distinguished by broken spotted spectral lines; the second by lines which are continuous and sharply resolved; and the third by lines which are broad and diffuse. The first class arises from a grain size greater than about 10^{-3} cm.; each spot on a line is the reflection from one grain so that the number of spots is a simple function of the number of grains in the volume illuminated by the incident X-ray beam. As the grain size decreases this number increases until the spots coalesce and form the normal sharp line; this gives the second class at a grain size of 10^{-3} to 10^{-4} cm. The third class occurs as the size of the grains diminishes to 10^{-5} cm. or less; then, the number of parallel atomic planes in a grain, on which the resolution of a given diffraction line solely depends, becomes too small for adequate resolving power; from the broadening of the lines the grain size can be estimated by formulæ developed by Scherrer, Seljakov and Laue.¹ The numerical limits of each class will vary somewhat with the experimental technique used; those given apply to normal dispositions employing analysing radiations of 1.5 to 2 Å.

Now the first class includes metals which have been annealed, and electrodeposited coatings of the softer type such as copper; the second class of spectrum includes metals as usually available, and is the most universal class; the third class is met with only in special cases, such as strain-hardened metals and alloys of the interstitial solid-solution type. The point is made that since it is in this third class that the spectra of nickel and chromium coatings invariably fall, they are abnormal. Actually, chromium coatings are outstanding in giving extremely diffuse lines. Measurements of the grain size of a number of specimens coated on copper from a chromic acid bath (25 per cent. CrO_3 , $\frac{1}{4}$ per cent. H_2SO_4) are given in Table I.; they are estimated from

¹ V. Laue, *Z. Krist.*, 1926, 64, 115.

the broadening of the (211) line with the aid of Laue's equations, and indicate the very fine grain obtainable.

Further evidence which suggests that the class of spectra given by these coatings is

abnormal arises from work on the X-ray spectra of cold-worked metals.² The latter, except for certain soft or spontaneously annealing metals, also show a broadening of the X-ray lines. But there is this difference: if the breadth of a given line is plotted against

TABLE I.—GRAIN SIZE OF ELECTROPLATED CHROMIUM COATINGS FROM CrO_3 BATH.

Current Density (m. amp./cm.) ²	Temperature.	Nature of Deposit.	Grain size (cm.).
50	30° C.	Bright	8×10^{-7}
100	"	Dull, dark grey	9×10^{-7}
150	"	"	10×10^{-7}
200	"	"	15×10^{-7}
250	"	"	19×10^{-7}
50	50° C.	Bright, smooth	10×10^{-7}
100	"	"	12×10^{-7}
150	"	"	13×10^{-7}
200	"	"	14×10^{-7}
250	"	"	14×10^{-7}

the percentage reduction in thickness as the annealed metal is, for example, cold-rolled, it is found that after increasing rapidly in the early stages of reduction the line-breadth tends to a definite limiting value. This limit is characteristic of the metal and independent of the mode of deformation. Measurements obtained in the cold-rolling of strip nickel are given in Table II.

TABLE II.—CHANGE IN BREADTH OF (311) LINE OF NICKEL ON COLD-ROLLING.

Reduction in Thickness.	Half-breadth.
Per cent.	mm.
3.9	0.29
12	0.57
22	0.86
29	1.14
37	1.14
42	1.29
48	1.00
53	1.00
58	1.14
63	1.14
68	1.00
73	1.00

Consequently, this limit differentiates the diffusion of the spectrum of the cold-worked metal from the apparently unlimited broadening obtainable from the electrodeposited coatings. The rate at which the line-breadth varies with cold-working of the metal is of further interest. The grain size of the initial annealed metal gives rise to spotted spectral lines of the class 1 type; but only 1 or 2 per cent. reduction in thickness is necessary to cause the metal to give the spectrum of class 2; and then the most stringent reduction will not do more than bring the grains on to the border of the third class. The ease with which the first breakdown occurs is consistent with the view that the original large grains contain a distribution of flaws at a statistical separation of about 10^{-4} cm., that is, at the distance corresponding to grain size in the second or usual class: the difficulty of diffusing the spectral lines indefinitely suggests that at ordinary temperatures there is a lower limit to the grain size to which a normal metal can be broken down.

Attempts to break down the grains below this limit must be countered by recrystallisation. But the feature distinguishing the electroplated nickel and chromium coatings from the normal or from the cold-worked

² W. A. Wood, *Phil. Mag.*, 1932, 14, 656.

material is that the former actually give a grain size much smaller than this limit. Therefore in order to maintain the subnormal grain size, the metal coatings must contain stresses sufficiently intense to inhibit grain growth and keep the grains in the third class. In the case of chromium and nickel this state may result from occluded oxygen and hydrogen atoms. It is of interest too that when the chromium lines are most diffuse one often finds in the spectrum traces of a hexagonal allotrope, suggesting that the cubic cell changes over to the hexagonal type to relieve the stresses. The allotrope disappears on heating. An analogous effect characterises the surface of alloy steels case-hardened by nitriding; these surfaces give extraordinarily diffuse spectra, and the cubic iron goes over to a hexagonal formation in the surface nitride. It is to be expected too that these stresses involve distortion of the atomic lattice. This is found to be the case as shown below.

2. Lattice Distortion.

Distortion of the lattice in the individual grains will also produce line-broadening. The permissible degree of distortion, from considerations of stability, must be limited; the amount of line-broadening associated with it will therefore be limited. On experimental grounds, the writer has suggested that maximum line-broadening produced by heavy cold-working of a metal represents the limit in question.³ If so, it can be determined for a given metal by measurements such as those in Table II.

Considering the spectra of the metallic coatings on this view we reach the following position: (i) if the line-broadening is less than that corresponding to the limit observed in the cold-worked metal, it may be due to lattice-distortion or fine grain; (ii) if the broadening is greater than that at the distortion-limit, it must be due, at least in part, to the fine grain effect; finally, (iii) only if the broadening is very large compared with the distortion limit can the latter be neglected and the broadening interpreted directly in terms of fine grain. This is the case for chromium coatings and justifies the application of the Laue equations in the measurements summarised in Table I. The line-breadths obtained for nickel however, are less, and might therefore necessitate corrections for the presence of distortion.

That lattice-distortion is present in the structure of nickel coatings is suggested by the following experiments. A series of measurements was made on the (311) line of nickel deposited on strip copper at various current densities from a nickel sulphate type of bath; these gave values of line-breadth varying, as expected, over a wide range. A second set of measurements was made on the same specimens after a reduction by cold-rolling which should, according to other data, induce the maximum broadening from lattice-distortion. It was considered that the process of working, by introducing lattice-distortion, as with ordinary nickel, should result in a further increase in breadth of the (311) line. An increase equivalent to the lattice-distortion limit would indicate that the original deposit was free from distortion; no change would mean that the original was already distorted to the limit; and an intermediate increase would occur if partial distortion were previously present. The results are summarised in Table III.; the line-breadths are measured under the same conditions as those in Table II.

³ W. A. Wood, *Nature*, 1933, 131, 842.

and with them they are comparable. It is seen that they show changes from zero upwards, the least change occurring when the original line is already broad; but there is no increase greater than can be explained by the introduction of lattice-distortion. The final breadth, less the broadening corresponding to the lattice-distortion limit, gives, other things being equal, that part of the original due to fine grain.

TABLE III.—BROADENING OF (311) LINE OF ELECTRO-PLATED NICKEL ON COLD-ROLLING.

Specimen.	Half-breadth (mm.).		Change.
	Before Rolling.	After Rolling	
a	0.4	1.1	Very large
b	0.7	1.1	Large
c	0.9	1.3	Large
d	1.0	1.9	Large
e	1.3	1.6	Small
f	1.4	1.6	Small
g	1.4	1.3	Zero
h	1.6	1.4	Zero
i	1.6	1.6	Zero

A further aspect of lattice-distortion is found particularly in nickel coatings. This produces a weakening of high-order reflections relative to the earlier orders; it is attributed to modifica-

tions in the scattering-power of the atoms. The effect is particularly marked when the nickel is photographed with copper $K\alpha$ radiation. The normal metal gives strong (311) and (420) lines; but the metallic coating gives the same lines abnormally weak, even when the influence of broadening is allowed for. This effect must be associated with a disturbance of the electronic configuration of the atoms. It is regarded as the preliminary to the grosser form of distortion which disturbs the atomic formation; it occurs also in aluminium which never shows line-broadening on deformation except at low temperatures.

Besides the above factors the X-ray spectrum often shows the further variable arising from selective crystallographic orientation of the grains composing the metallic coatings.

3. Selective Orientation.

In normal material the grains are oriented at random; therefore the spectrum lines possess a definite intensity distribution. Under the directive forces producing deposition, the grains tend to grow with a given crystallographic axis in a preferred direction; the intensity distribution then departs from the normal. The degree and sometimes the type of the preferred orientation vary greatly with conditions of deposition. In the case of deposition on a surface already selectively oriented, the writer found that the coating tended to follow the orientation of the base if the two metals were the same; but if different the metals took up the same orientation only under steady critical conditions of deposition.⁴

Attempts have been made to associate the changes in degree of orientation with changes in the hardness of the metal. But it is the writer's experience that no consistent relation can be established. This agrees with observations on the hardening of cold-worked metals where it is found, for instance, that as an initially annealed metal is

⁴ W. A. Wood, *Proc. Phys. Soc.*, 1930, **43**, 138.

progressively cold-rolled, the selective orientation appears and grows most rapidly long after the main increases in hardness have taken place. Arising out of the examination of nickel and chromium coatings to test this point there was found, however, (a) a relation between the perfection of the orientation and the brightness of a deposit as taken from the bath, and (b) a relation between the hardness of the coatings and the line-broadening of the spectral lines.

Thus, taking the first relation, the chromium coatings varied from a dark grey deposit to one of high metallic lustre according to the temperature and current density at which the CrO_3 bath was worked. In ten bright deposits on copper obtained at 50°C . with current densities of 25 to 500 milliamp./cm.², the (200) spectrum line was practically absent and the (211) very strong, a marked departure from the normal intensity ratio. In ten deposits of the dull type obtained at 15°C ., and measured under the same conditions as before, the intensity ratio was found to be normal. The same result was shown by nickel coatings on copper from the nickel sulphate and the nickel ammonium sulphate type of bath. In this case the ratio of the (200) to the (111) intensities along the equatorial line of the photographs was determined. The ratio varied from values where the (111) was stronger than the (200) reflection to values where the (111) was weaker. Of twenty specimens examined the brightness was greater the departure from the normal intensity ratio, that is, the more perfect the orientation.

4. Hardness and Line-broadening.

As stated, it was found that if the metallic coatings were placed in order of hardness, the X-ray spectra varied regularly in degree of diffusion; the softer coatings corresponded with sharp spectral lines and the harder with broad lines. It is desired to point out that this example of the electroplated coatings does not form an isolated case; it falls into line with so many other examples noted during the last few years that the association can hardly be fortuitous. If the change in hardness is large, the effect may be very pronounced. This is actually the case with chromium coatings: the (211) line of the spectrum, obtained with $\text{Cr } K\alpha$ radiation, changes from the sharp doublet characterising the spectrum of the normal metal to a broad band almost 1 cm. wide when obtained from the electroplate; at the same time the hardness goes up to 1000 Brinell. A further striking example is supplied by the surface of the special steels casehardened by the nitriding process: it was found that the (220) lines of the steel, though obtainable strong and sharp in the spectrum from the interior or the untreated steel, diffused so much as to become almost invisible in the spectrum from the case-hardened surface; at the same time, the hardness value increased from 280 Brinell for the untreated steel to 1200 for the nitrided surface; and intermediate steps in the hardening corresponded to intermediate degrees in the line-broadening.⁵ Further examples have arisen in results on tungsten magnet steels,⁶ stainless steels,⁷ cold-rolled metals. It may be that the X-ray spectrum, in the present stage of technique, is not sensitive to small changes of hardness; but it certainly appears that large changes in hardness in a given structure

⁵ W. A. Wood, *Phil. Mag.*, 1933, 14, 719.

⁶ *Ibid.*, 1932, 13, 355.

⁷ *Ibid.*, 1930, 10, 1073.

type produce gross diffusion of the spectrum. And to this generalisation, the nickel and chromium coatings form no exception.

An explanation of the hardness in terms of grain size and distortion might be made on the view that these factors present centres of dislocation tending to resist deformation of the lattice by the recognised means. It should be noted that the two factors, when the grain size is very small, are physically equivalent. For the surface cells of a grain must be subject to disturbance, and the smaller the grains the greater will be the volume occupied by the distorted surface layers. Thus in the case of the chromium coatings, a distorted surface only one unit cell in depth, would represent about 20 per cent. of the whole volume of a grain. The excessive broadening of the X-ray lines, therefore, though primarily due to the fine grain effect, is an overall measure of disturbance in the lattice. It is suggested that this disturbance is associated with that part of a hardness value which measures resistance to plastic deformation.

Summary.

The features distinguishing the X-ray spectrum of an electrodeposited metallic coating from that of the normal metal are discussed in terms of the changes in structure thereby indicated. Relations between the selective orientation and brightness of nickel and chromium coatings are noted. Also attention is drawn to the diffusion of the spectral lines of these coatings, and to a correspondence between the line-broadening and the hardness of the deposits.

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THE STRUCTURE OF ELECTROLYTIC CHROMIUM.

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Some confusion exists in the literature as to where and when the first announcement was made of the electrodeposition of a hexagonal modification of chromium.

Sillers¹ gave priority to Ollard,² and subsequent workers have agreed with him, but this is incorrect.

The first mention of the production of a hexagonal modification was made by Bradley and Ollard.³ This statement appeared on 23rd January, 1926, whilst Ollard's remarks were part of a more general paper which was not read until 12th February, 1926. Bradley and Ollard said that their chromium was prepared by a special method, details of which were not given. Neither were details given as to the percentage of the hexagonal form present, but one of the authors⁴ has told us recently that the specimens examined contained about 90 per cent. of the hexagonal form. They published no photographs of the structure but described it as being almost hexagonal close-packed with an axial ratio $c/a = 1.625$ and distance between neighbouring atomic centres 2.714 \AA . They

attributed to this modification peculiar properties which were dealt with at greater length by Ollard² who thought that the excessive hardness of the samples was probably due to the hexagonal modification. No data was given concerning its production other than that it was obtained from chromic acid solutions.

McNaughton,⁵ discussing Ollard's paper, confirmed the existence of a hexagonal form, but gave no data concerning its production or structure. He found a softer dark deposit to contain about 85 per cent. of the hexagonal form but a harder bright deposit contained only a trace of the hexagonal modification. He did not agree that the hardness of the deposited chromium was due to the presence of the hexagonal form.

Ollard⁷ in a subsequent paper added to the known properties of electro-deposited chromium, but gave no details which had any bearing on the production of the hexagonal form. He pointed out that this structure was associated with much hydrogen and commented on the smallness of the crystals found in the deposits which possessed a brinell hardness figure of 900. He found that upon annealing, the specimens became softer but attributed this to a change in grain size.

The appearance of Smith's⁶ work, in which he found no existence of the hexagonal form, was not unexpected, in view of the complete lack of data relative to its production. He electrolysed a solution of chromic sulphate and one containing chromic acid (160 g./L.), chromic sulphate (5 g./L.), saturated with chromic hydroxide. From both solutions he obtained deposits which possessed only the body-centred cubic structure. He suggested that possibly Ollard's conditions had differed from his and that the hexagonal form might be due to the presence of a hydride of sufficient stability to possess a definite lattice of its own. In reply, Ollard⁸ stated that it depended entirely on the method of deposition as to whether the hexagonal or body-centred cubic was obtained, and that upon heating at quite low temperatures the hexagonal form could be converted into the body-centred cubic with evolution of large quantities of hydrogen. He could not say, however, whether a definite hydride existed. No particular degree of hardness could be associated with either form since each could be produced equally hard and each possessed similar mechanical properties.

Sillers¹ examined both grey and bright deposits but found no indications of a second or allotropic modification of chromium. These deposits were obtained in the manner suggested by Haring⁹ in which a solution of chromic acid (250 g./L.), chromic sulphate (3 g./L.), and chromium carbonate (7 g./L.) was electrolysed at 100 amps./sq. ft. with a lead anode. The chromium was deposited on to brass sheets which were subsequently dissolved, leaving the pure chromium which had a lattice parameter value of 2.872 ± 0.005 Å.

Ollard, in a contribution to the discussion on Siller's paper, stated that the hexagonal form could only be obtained when the solution was operated in the cold and at a very high current density. He had obtained most of his samples of chromium as heavy deposits 3.2 mm. thick on a steel cathode from which the chromium was easily removed since it was brittle and readily powdered.

Sillers followed out Ollard's instructions and electrolysed a solution containing 250 g./L. CrO_3 and 2.5 g./L. H_2SO_4 at 5° C. and at a current density of 100 amps./sq. dm., but was unable to obtain the hexagonal form.

Sasaki and Sekito¹⁰ confirmed the existence of the hexagonal modi-

fication of chromium, but their deposits were obtained from solutions of chromium sulphate. They gave for the axial ratio c/a 1.626 and for the distance between atomic centres 2.717 Å. and confirmed Ollard's statement that the hexagonal modification was converted to the body-centred cubic on heating.

Wood¹¹ electrolysed a 50 per cent. solution of chromic acid containing $\frac{1}{4}$ per cent. sulphuric acid, in which part of the chromic acid had been reduced by the addition of a little sugar. From such a solution he obtained deposits which contained varying amounts of the hexagonal form. No photographs or data concerning the structure of the hexagonal form were given, but he showed that the amount present varied with both current density and temperature. From baths which had not been reduced he obtained only the body-centred cubic structure and suggested that before the hexagonal form could be deposited baths must first be reduced.

Sasaki and Sekito,¹² in a further paper, confirmed their previous findings, but were unable to obtain the hexagonal form from chromic acid solutions from which they obtained only the body-centred cubic structure with a lattice constant equal to 2.877 ± 0.003 Å.

Data concerning the structure of deposits obtained from chromic acid solutions by the various investigators are given in Table I:—

TABLE I.—DEPOSITS OBTAINED FROM CHROMIC ACID SOLUTIONS.

Investigator.	Type of Deposit.	Body-centred Cubic.	Hexagonal.	
		Lattice Constant.	c/a .	Distance between Atomic Centres.
Bradley and Ollard .	Mixed	—	1.625	2.714 Å
McNaughton . . .	Mixed	—	—	—
Smith	Body-centred cube	2.864 Å	—	—
Sillers	Body-centred cube	$2.872 \pm .005$ Å	—	—
Wood	Mixed	—	—	—
Sasaki and Sekito .	Body-centred cube	$2.877 \pm .003$ Å	—	—

It can be seen from Table I that for deposits from chromic acid solutions the only data concerning the structure of the hexagonal form is that given by Bradley and Ollard.

The values given by Sasaki and Sekito¹⁰ are in close agreement with those of Bradley and Ollard, but were not obtained for deposits from chromic acid solutions.

Wood¹¹ concluded that part of the chromic acid must be reduced, and this condition was certainly fulfilled by Bradley and Ollard although it was never mentioned.⁴ Although Wood appeared to be aware of the necessity of reduction to obtain the hexagonal form he gave no figures limiting the amount which should be present.

In view of the lack of agreement between the various investigators it was thought desirable to determine the conditions for the production of the hexagonal form from chromic acid solutions and to determine its structural constants.

Experimental Procedure.

Materials.

Commercially pure chromic acid was employed which was shown to have a sulphate content of 0.106 per cent. and this amount was allowed for when the solutions were made up to a specified normality. The methods of analysis were those employed by Moore and Blum.¹² The ultimate sulphate contents were obtained by the addition of pure sulphuric acid.

A number of methods were employed to obtain solutions containing

trivalent chromium, namely, reduction with hydrogen peroxide, tartaric acid and cane sugar. Conductivity measurements of chromic acid solutions reduced by equivalent amounts of the above mentioned reducing agents were in close agreement. For ease of control of the reaction all solutions used in this investigation were reduced with sugar.

Ollard¹⁴ plotted the specific conductivities of a reduced solution against the percentage of chromium contained in the cation. Similar curves are shown in Fig. 1 for solutions of 600 g/L and 175 g/L. The 600 g/L

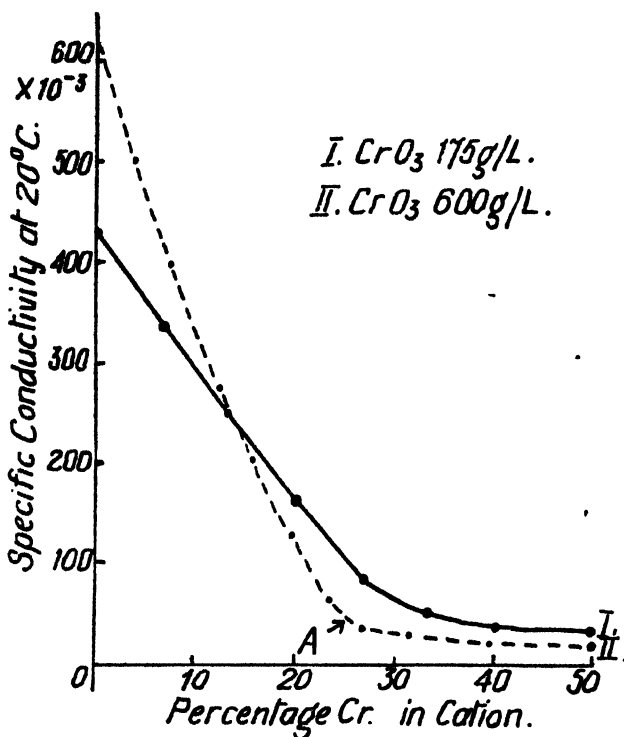


FIG. 1.

was that solution employed by Ollard¹⁴ whilst the lower concentration was that used in the course of this investigation.

Preparation of Deposit.

The chromium was deposited on to an aluminium wire 0.16 cms. in diameter which was immersed in the solution to a depth of 10 cms. Before plating the aluminium was freed from grease and well rinsed. The anode was in the form of a cylinder 10 cms. in diameter and was of chemically pure lead. The volume of electrolyte employed was 1 litre and this was contained in a glass vessel surrounded by a water bath which enabled the electrolyte temperature to be controlled to $\pm 1^\circ \text{C}$. All solutions employed contained 175 g/L CrO_3 , but the detailed composition is given later in Tables II and III. The electrode distance between anode and cathode was maintained constant throughout the experiments, and the duration, of deposition was also maintained constant, namely, two hours.

X-Ray Examination of the Deposits.

A Debye-Scherrer powder photograph was taken of each specimen. To avoid disturbing the chromium layer the aluminium wires were mounted directly in the X-ray camera. Monochromatic chromium radiation was used, the β radiation being absorbed by a filter of vanadium pentoxide. The conditions were the same for each exposure, namely, 43 kilovolts, 28 milliamperes for one hour. The developing and fixing of the films took place at the same uniform temperature. Tables II and III show the solutions employed together with the type of structure obtained for each deposit.

TABLE II.

Specimen.	SO ₄ Normality	C D amps /dm ² .	Temp.	Structure.
1	0.05	10.75	16° C.	Body centred cubic.
2	0.075	10.75	"	" " "
3	0.1	10.75	"	" " "
4	0.15	10.75	"	" " "
5	0.20	10.75	"	" " "
6	0.20	13.5	16° C.	" " "
7	0.20	16.25	"	" " "
8	0.30	10.75	16° C.	No deposit.
9	0.30	13.5	"	Body centred cubic.
10	0.075	13.5	16° C.	Body centred cubic.
11	0.075	16.25	"	" " "
12	0.075	18.75	"	" " "
13	0.075	21.5	"	" " "
14	0.075	27.0	"	" " "
15	0.075	32.25	"	" " "
16	0.075	10.75	25° C.	Body centred cubic.
17	0.075	10.75	40° C.	" " "

TABLE III.

Specimen	SO ₄ Normality	Per cent Cr. in Cathode	C D amps /dm ² .	Temp	Structure
18	0.075	*13.30	10.75	16° C.	Body centred cubic.
19	0.075	13.30	10.75	"	" " "
20	0.075	16.03	10.75	"	" " "
21	0.075	18.70	10.75	16° C	Body centred cubic + Hexagonal
22	0.075	20.04	10.75	"	Hexagonal
23	0.075	26.72	10.75	"	"

The photographs of the chromium deposits prepared from solutions containing no reduction content (specimens 1-17) showed the normal body centred cubic structure (*cf.* Plate I, Fig. 1). The lines were broad, due both to the small grain size and the internal stress usually present in electrodeposited metal. For specimens 13, 14 and 15, increase in the current density used led to a comparative decrease in the intensity of line.¹⁰ The hexagonal modification was found only in deposits obtained from

* Reduction with tartaric acid—others with cane sugar.

solutions containing over 18 per cent. of chromium in the cation. At the concentration it was found associated with the normal body centred cubic form (*cf.* Plate I, Fig. 2), but increase in the reduction content led to elimination of the body centred cubic modification.

The hexagonal modification (*cf.* Plate I, Fig. 3) was the one observed by Bradley and Ollard⁹ and Sasaki and Sekito.¹⁰ The distance between neighbouring atomic centres was found to be 2.717 Å. the axial ratio c/a being 1.626. The diffraction lines are broad, though not so much as those due to the cubic structure.

Further increase in the reduction content beyond 20 per cent. and increase in current density produced no further change in the structure.

A sample of the hexagonal allotrope was heated at 800° C. *in vacuo* for 1½ hours. An X-ray photograph then showed the structure to have been converted entirely into the body centred modification. The structure is exactly the same as that of the body centred cubic specimen (No. II) after heating *in vacuo*, also at 800° C. for 1½ hours (*cf.* Plate I, Fig. 4).

The value of the lattice constant for the heat treated body centred cubic and hexagonal structures is 2.8788 Å.

A sample of commercial chromium (99.15 per cent. pure) gave a value of 2.8781 Å. which differs by an amount considerably greater than the experimental error of the calculating method employed.¹¹

Discussion of Results.

In the absence of reduction content in the solutions only the body centred cubic modification was obtained; apart from some degree of preferred orientation the presence of the normal structure does not appear to be influenced by any change in current density, temperature, or alteration in the ratio of chromic acid to sulphate content. The amount of chromium in the cation influences the formation of the hexagonal allotrope and a certain minimum of trivalent chromium must be present.

The use of high concentrations of chromic acid and the employment of high current densities were not essential for its production. Ollard¹⁴ and Kaspar¹⁶ have described the formation of reduction compounds in chromic acid solutions and have allotted formulæ to compounds corresponding to certain degrees of reduction.

When 25 per cent. of the chromium exists in the cation Kaspar¹⁶ assumes that the solution consists of chromium dichromate $\text{Cr}_2(\text{Cr}_2\text{O}_7)_3$. In Fig. 1 and curve II the point A, corresponding to this degree of reduction, occurs where a distinct change in the slope of curve occurs, but with curve I a similar change in the slope of the curve is associated with a higher reduction content. Kaspar¹⁶ showed chromium dichromate to be a strong electrolyte and dilution of the chromic acid solution would account for this delayed alteration in the slope of curve I.

Specimens wholly hexagonal were produced in solutions containing 20 per cent. chromium in the cation, but for this percentage reduction no marked alteration occurs in the slope of the curves. It does not appear possible to attribute the formation of the hexagonal modification to a solution consisting entirely of any known reduction compounds.

Conclusions.

The existence of the hexagonal modification of chromium in deposits obtained from chromic acid solutions has been confirmed. The distance between neighbouring atomic centres is 2.717 Å. the axial ratio c/a being 1.626.

Deposits may exist comprising wholly the body-centred cubic form, the hexagonal form or mixtures of both.

The hexagonal form was converted to the body-centred cubic on heating in vacuo at 800° C. for 1½ hours, and was then found to possess a structure identical with a body-centred cubic specimen treated under similar conditions.

The value of the lattice constant for such heat-treated structures was 2.8788 Å., as compared with 2.8781 Å. for a sample of commercial chromium (99.15 per cent. purity). It has been shown that the factor influencing the formation of the hexagonal allotrope is the percentage of chromium existing in the cation in reduced chromic acid solutions.

The absence of sufficient trivalent chromium in the chromic acid solutions used by other investigators was undoubtedly the primary reason for their failure to obtain the hexagonal allotrope.

Deposition at room temperature in the absence of the required minimum reduction content yielded only the body-centred cubic structure. The structure was found to be independent of the reducing agent employed. The broadening of the diffraction lines is more marked in the case of the body-centred cubic than the hexagonal structure.

This effect can be removed by heat treatment of the deposit, but since this leads to removal of the stress as well as increase in grain size the authors cannot agree with Wood¹¹ that it is due entirely to the smallness of grain size. Further work is in progress to determine to what extent the broadening of the lines is due to internal stress in the deposits.

The authors wish to thank Mr. A. P. M. Fleming, C.B.E., Director, Manager of the Research and Education Departments, Metropolitan-Vickers Electrical Co. Ltd., Trafford Park, for permission to publish this work.

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GENERAL DISCUSSION.

Dr. H. J. T. Ellingham (*London*) said that Dr. Glasstone's objection to the theory that metal deposition from complex cyanide solutions occurred by discharge of simple metallic cations was not a vital one, since, although electrode potential measurements led to extremely low values for the concentrations of the simple cations in such solutions, these values should be regarded as representing the

fraction of the life of a metal atom spent in the form of a simple cation : from this point of view the values were not absurdly small. On the other hand, Dr. Glasstone's views regarding the existence and discharge of complex cations in these solutions were of great interest, and certainly served to explain a number of facts in a simple fashion. Since complex cyanide solutions probably all contain some of the metallic cyanide in colloidal form, it might well be that still more complex cations, micelles in fact, were present in them. This would seem to be a legitimate extension of Dr. Glasstone's theory.

The results of Mr. Wood were of particular interest in showing how X-ray methods could be applied to the study of the structure of electro-deposited coatings. It was to be hoped that Professor Finch or other exponents of electron diffraction would give further indication as to how far their method was likely to be able to distinguish between the various types of contamination of electro-deposited metals with oxide or other compounds which had been suggested in the course of this Discussion, *e.g.* to distinguish between impurities present along grain boundaries, forming true solid solutions with the metal, or intruded into the metal lattice producing deformation : also it would be useful to have some idea as to what proportion of such impurity would have to be present in order to be detectable. So many of the papers before the meeting had contained reference to possible effects of sparingly soluble compounds of a metal on the structure of its electro-deposited coatings, that it was clear that the question was of outstanding importance in the development of the theory of the metal deposition process ; and any information on this subject which could be obtained by the various methods now available for the examination of the structure of metallic films would be of the greatest value.

Dr. L. Tronstad (*Trondheim*) said : It is essential to distinguish between two entirely different kinds of impurities : (1) Those present in solid solution in the metal, which widely affect certain metal properties as electrical conductivity, etc. (2) Those present as indigenous or exogenous inclusions, which may modify other metallic properties (*e.g.* corrosion resistance, etc.). Impurities of type 1 may be detected directly or indirectly by electron- or X-rays, but those of type 2 (especially in the case of traces of non-metallic inclusions) may most conveniently be examined by chemical, *i.e.* microanalytical means. Several methods for microanalytical examination of inclusions in metals have been developed during the last years, among which the "printing-methods" and the "needle-electrode" seem to be most useful.

Professor A. Glazunov (*Pribram*) said : In case of cadmium electrolysis cv_I and cv_{II} are very sensitive as to the current density ; crystals in the form of needles were observed in the case of cadmium plating of copper wire on the side near the anode, whereas on the other side (where the current density was smaller) the coating was continuous.

Professor L. S. Ornstein (*Utrecht*) said : It is certain that in crystalline matter strong deviations of structure are possible in pure metals. Optical research on the fine structure of the Rayleigh scattering in crystals has shewn that a component of unchanged wavelength exists which should be absent in an ideal crystal. Van Cittert and Ornstein have shown that this component is due to small distortions which are present in even the best sample of crystal.

As a method of investigation, magnetic measurement seems very important, inclusions of oxides and dissolved oxygen must strongly

influence the magnetic properties; how far has such work been done?

In the Utrecht Institute Mr. Baars has investigated the etching of electrolytic copper by iron chloride. The formation of surface layers of great importance in this process can be followed by potential measurement at definite concentrations; polygonical etch forms are obtained which are not crystals of copper, but are induced by the formation of surface layers of CuO . These types of reaction seem of importance for some of the phenomena treated by the different metallurgists.

Dr. W. Blum (*Washington*) said: The simplest form of the generalisation of Blum and Rawdon is that "other conditions equal, the cathode potential is an important factor in crystal structure," actually, it is very difficult to greatly change the cathode potential without also changing other factors, such as the conductivity, the concentrations of other ions, and the tendency for precipitation of basic materials. It is believed, however, that even with these limitations, the generalisation may be usefully applied.

Many apparently minor factors may influence the structure of electrodeposits and their relation to the structure of the base metal. For example, some years ago Foerster reported that when tin was deposited from stannous sulphate upon an etched tin surface, the "flowers" in the latter were not reproduced. If, however, cresylic acid was added to the solution, the deposit reproduced the structure of the base metal. It seems probable that this difference is caused by the cresylic acid retarding the precipitation of stannous hydroxide at the cathode, which, if precipitated, would interfere with crystal growth.

Dr. S. Wernick (*London*) said: Dr. Glasstone's view of the ionisation of the complex double cyanide provides an interesting explanation of the fine-grained deposits which such baths usually produced. While such a theory is not untenable, it seems that a more fruitful line of thought is one which explores the possibility of colloidal presence in the electrolyte and the known characteristic of colloids under favourable conditions to exercise interference at the cathode interface with the process of crystal growth.

It is a well-known fact among electro-platers, who are in perhaps the closest contact with the practical phenomena which arise in the continuous electrodeposition of metals, that freshly prepared plating solutions of the single sulphate type do not work well. Such new solutions usually produce deposits which are dark or non-uniform (in the case of nickel, for example) or relatively coarsely crystalline (as in the case of zinc deposits). White, uniform and closely-grained crystalline deposits are often eventually obtainable from such solutions after they have been worked for some time or, in other words, "aged." To achieve this result as rapidly as possible, it is quite common practice to use scrap metal as cathodes and pass a continuous, relatively heavy current through the electrolyte, in order to accelerate the "ageing."

It is noticeable that such "ageing" methods are not usually required in the case of complex electrolytes, such as cyanides, from which deposits of good quality are readily obtainable as soon as the solution is prepared.

These facts are highly suggestive of colloidal action. One may assume absence of colloids in the simple sulphate type of electrolyte, which therefore require to be introduced in the electrolyte by working or ageing the solution, while such a procedure is unnecessary where

complexes capable of producing colloidal matter are already present, as in cyanide electrolytes. It is noteworthy that most "complex" electrolytes, whether they are cyanides, double sulphates, fluo-silicates or even perchlorates, are capable of readily producing finely-grained deposits.

In the case of cyanide solutions which are used for the production not only of silver, but also copper, zinc, cadmium and other deposits, it is suggested that some form of polymerisation of the cyanide radicle occurs at the cathode interface, resulting eventually in the formation of particles not of atomic but of colloidal dimensions, which then form a net-work over the cathode which interferes with the process of deposition. The interference is one which probably tends to prevent growth of individual crystals and to encourage the formation of the largest number of crystal nuclei. The exact mechanism is open to conjecture, but the general theory outlined above seems to fit in with the known facts and does not appear to have any serious objections.

DETERMINATION OF THE PHASE STRUCTURE OF METALLIC PROTECTIVE COATINGS BY ANODIC DISSOLUTION.

BY A. GLAZUNOV.

Received 31st January, 1935.

All metallic protective coatings may be divided into two groups :

1. The potential of the protective coating is smaller than the potential of the base metal.
2. The potential of the protective coating is higher than the potential of the base metal.

It is obvious that whether the coating of a metal may belong to the first or second group depends on the potential of the base metal.

Coatings of the first kind must be continuous and not only sufficiently thick but, in each case, of an even thickness. A coating which in some places is quite thick and in others thin is useless. It results from this that the coating of the first kind protects only so long as the base metal does not come into contact with external factors, *i.e.*, only so long as it has a minimal thickness.

It is of little importance with coatings of the second kind whether there are cracks or pinholes ; moreover it is not the minimal thickness but the average thickness (that is, the quantity of metal may be sacrificed for the protection of the base metal), which matters. In addition, adherence to the base metal and resistance of both kinds of coatings to mechanical deformation is important ; *e.g.*, they must not crack on bending. The last-mentioned property depends upon the contact between the base metal and the protective metal and also upon the thickness of the intermediate layer of chemical compounds and solid solutions, these latter being generally brittle.

Analytical methods of testing may reveal the composition of these coatings.*

If the coatings are complex, it is difficult to determine their composition even qualitatively, *e.g.*, when the base metal contains a small quantity of the elements which constitute a substantial part of the coating. As an example we may mention nickel-steel covered with a nickel-chromium coating. Arnold has recently proposed the use of a spot method, as well as the electrographic method of the author, in this way he realised a very good, simple, and quick chemical method of testing metallic coatings without destruction of the sample. In this way the question of chemical testing of coatings may be considered as solved.

As regards the thickness of the metallic coatings (*i.e.*, of the pure metal as well as of the intermediate layer) we may resort in many cases to metallography (*i.e.* to the intermediate measurement of these layers, after etching, under the metallographic microscope).

Almost all the methods for determining the thickness of metallic coatings ascertain only the *total* thickness of the coating and only rarely the thickness of the intermediate layer. None of these methods serve to determine the thickness and composition of different phases of the intermediate layer. All these tests are insufficient, in that they prove the quality of the coating only relatively and, moreover, most of them are somewhat complicated.

The author submitted to the XII. Congress of Applied Chemistry in Praha, 1932, a new method for determining the thickness and quality of the spelter coating on iron (of the second kind).

The method is based on anodic dissolution of the galvanised sample † by such conditions that the cathodic process as well as the resistance of the bath remain constant during the test.

The total voltage of the electrolytic bath consists of the potentials (1) of the anodic process, (2) of the cathodic process, and (3) that which is necessary to overcome the resistance of the bath, *i.e.*,

$$\begin{aligned} E &= E_K + E_A + I \cdot R, \text{ working with the insoluble anode,} \\ E &= E_K - E_A + I \cdot R, \quad \text{,,} \quad \text{,,} \quad \text{,,} \text{ soluble anode.} \end{aligned}$$

If E_K and $I \cdot R$ are constant, all changes in the potential will be due to the changes of E_A . When we have a soluble anode, the factor E_A will depend on its chemical composition. So long as the chemical composition of the ions passing to the electrolyte is constant, there will be no change in the factor E_A and the potential will remain constant. When the composition of the soluble anode changes, however, E_A will change also, and, thus the total E also.

In the case of galvanised iron in a zinc salt solution the potential will remain constant, so long only as a layer of pure zinc dissolves, *i.e.*, $E_A = E_K$ and the total $E = I \cdot R$. Should dissolution of the intermediate layer (composed of various products of interaction between zinc and iron) take place, the potential will rise (because $E_A < E_K$)

* This is quite important, since of late electroplating by alloys has been much used, but they cannot answer all the questions as to the property of the coatings. Chemical tests of coatings are not simple for, with the wide use of electroplating, the coating is often so thin that it is difficult to determine it quantitatively by the ordinary methods of analytical chemistry.

† By the change of potential on dissolving galvanised coatings in hydrochloric acid, Evans was able to determine whether the coated object is an electroplated, a hot-dipped, or a sherardised wire.

until it stabilises itself at a value corresponding with the process of dissolution of iron.

Whatever was the method used for coating, diffusion between the metal of the protective coating and the base metal will always take place and there results an intermediate layer composed of various phases, which may be formed according to the thermal diagram.

It is obvious that with different methods of plating the thickness of the intermediate layer as well as its phase structure will differ. In processes which take place at higher temperatures, the intermediate layer will be thicker and, sometimes, there will be no layer of pure protective metal; in electroplating (at lower temperatures) the layer of intermediate products will be minimal. It will nevertheless exist in both cases.

In determining the thickness of the coating by the method of anodic dissolution the thickness of coatings of individual phases will be quite apparent; for each phase of constant composition has its own potential. During its dissolution the potential will be constant. When dissolving a phase of changing composition (solid solution) the potential will change periodically in accordance with the potentials of the limit concentrations of the solid solution in question. The current curve will be the reciprocal of the potential curve.

The lengths of the individual potential values (horizontal positions of the curve) and of the intervals between them will show the quantum of the individual phases and their composition if we know the course of the potential curves of the binary system in question.

To attain a constant value for $I \cdot R$ and E_K we use, as electrolyte,

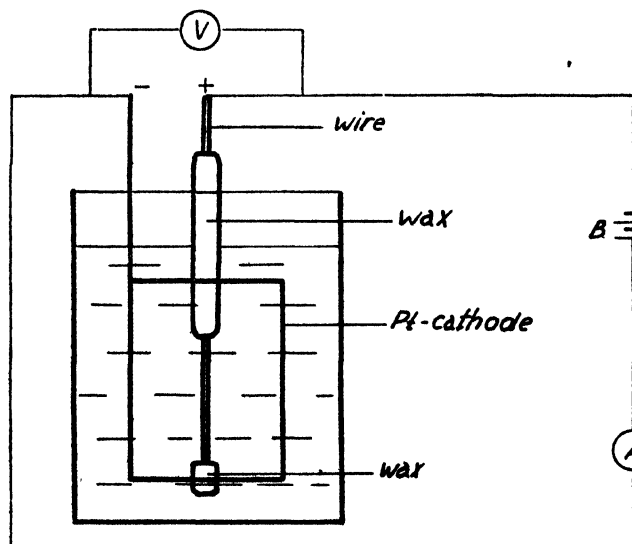


FIG. 1.

the concentrated solution of some simple salt of the metal in question; for example, with galvanised objects zinc sulphate solution gives very good results. The cathodic process will proceed during the whole experiment, accompanied by deposition of zinc (*i. e.*

$E_K = \text{const.}$) and the bath resistance also will be constant. The short time of the experiments (for a normal coating thickness solution usually takes five to six minutes) and the small distance between the electrodes makes it practically impossible to form the concentration cell.

The amount of iron entering into the electrolyte during the solution of the intermediate layer, also, does not affect the cathodic process,

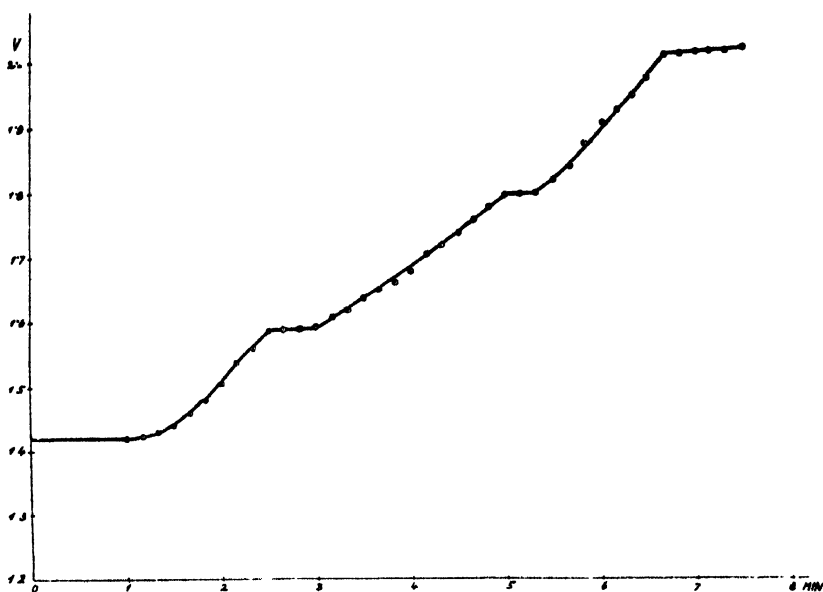


FIG. 3.

for, when using a concentrated solution of zinc salt, the amount of iron is usually insufficient to bring about a change in the potential in the cathode.

The scheme of the apparatus is illustrated in Fig. 1 for wires, for coated sheets the difference will be only in the form of the cathode. To study the coating the samples are so arranged that, except for a small part of the surface, the sample is covered with wax or some other substance preventing its contact with the electrolyte. A group of wires, ready for investigation, is shown

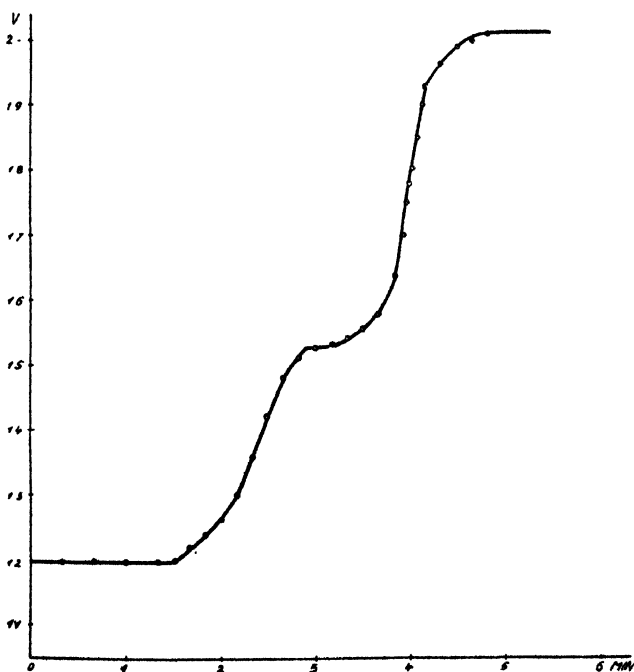


FIG. 4.

in Fig. 2.* In these experiments we measure the current. If we know the surface of the sample, the amperage and the time, we can easily calculate the thickness of the coating, according to the following formula :

$$d = \frac{e \cdot I \cdot t}{\eta \cdot s},$$

where d = thickness of the layer, e = electrochemical equivalent, I = intensity of the current, t = time, η = specific gravity of the metal, s = surface.

Individual phases have their own η which will be used in these calculations. If η for the individual phases is unknown we shall not err much if we take a value for the mechanical mixture of the two metals, corresponding to the composition of the phase in question.

If, for instance, we take a galvanised iron wire then, depending upon the manner in which zinc was coated, we shall get altogether different diagrams of anodic dissolving. Examples of the curves for zinc coated

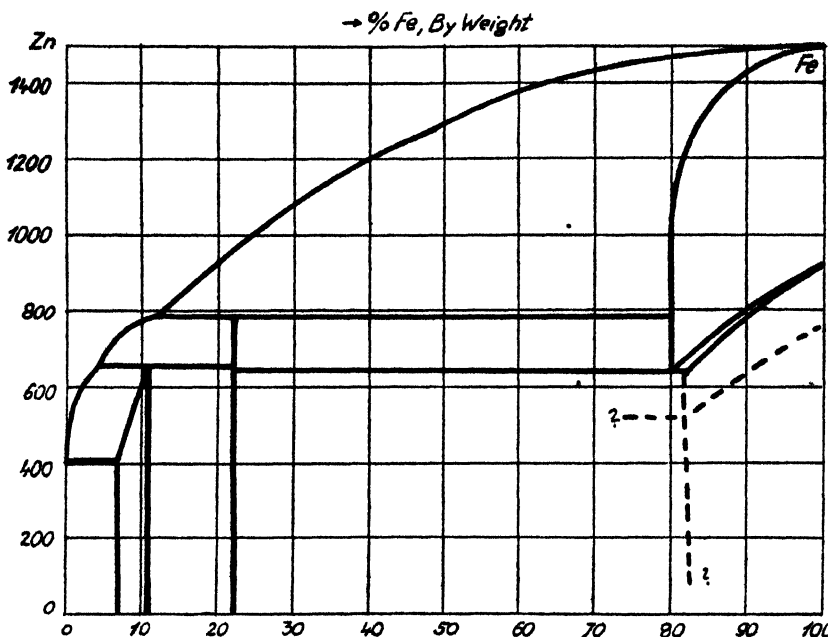


FIG. 5.

wires by hot-dipped iron are shown in Fig. 3, and curves for wire coated with zinc by electroplating process in Fig. 4.

A thermal diagram for Zn-Fe according to Raydt and Tammann, Vegesack and Peirce, and a potential diagram according to Vigouroux, Ducelliez and Bourbon are shown in Figs. 5 and 6.

Naturally these diagrams do not entirely agree since, for the sudden change of potential at 75 atomic per cent. Fe, there is no marked chemical compound, Fe_2Zn ; probably the decomposing compound has escaped the attention of investigators. From 81 atomic per cent. Fe to the potential of pure Fe there should be an interrupted convex curve.

If we compare the resulting curves with the potential diagram we see that the intermediate layer with galvanised iron and also with the electroplated iron is composed of several phases, especially of the phases of Zn_2Fe and ZnFe_3 (?) by hot-dipped plating and ZnFe_3 (?) by electroplating. Some deviations in the numerical differences of the heights of potentials

between the individual phases are due to the fact that the working conditions, in our experiments and those by which the potentials of the system

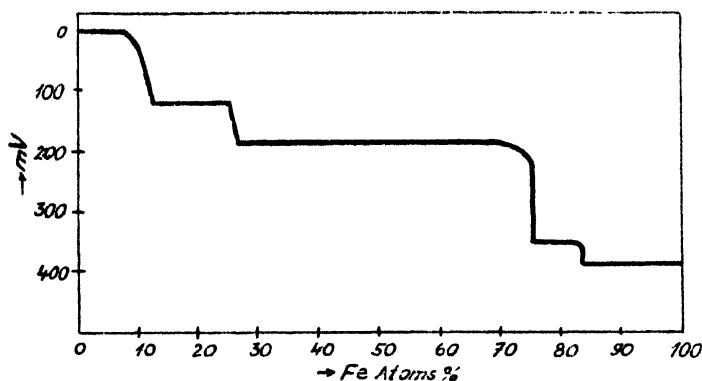


FIG. 6.

Fe-Zn have been determined, were different. Naturally, in the hot-dipped process the extent of these phases is much greater.

For technical purposes it is generally sufficient to determine only the thickness of the intermediate layers regardless of the individual phases—in this case we consider the curve of the anodic dissolution of the intermediate layer to be unbroken.

The curve of the anodic dissolution of nickel-coated copper is another example. Copper and nickel give together a solid solution in all proportions. The form of the curve is shown in Fig. 7. As may be seen the course of change of potentials in the intervals of the intermediate layer is unbroken.

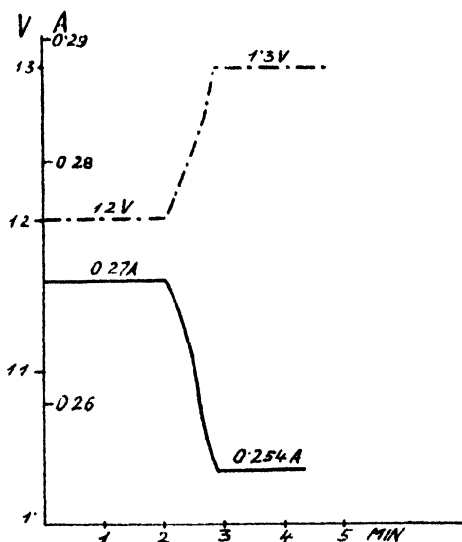


FIG. 7.

Conclusions.

1. In cases where the base metal is protected at the expense of the coating, the author's method of anodic dissolution serves to test not only the thickness of the whole coating or even of the intermediate layer, but also to ascertain what phases compose this intermediate layer and to determine the thickness of the individual phases.

2. By this method, it is also possible very easily and quickly to ascertain the method used in metal coating.

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IMPROVEMENT OF THE QUALITY OF SPRAYED METALLIC COATINGS BY THE USE OF NON-METALLIC INTERMEDIARIES AND SUPPORTS.

BY H. REININGER, LEIPZIG.

Received in German 15th March, 1935, and translated by
DR. E. A. RABINOWITCH.

Metallic coatings produced either by galvanisation or by spraying are never very firmly bound to the base-metal on which they have been deposited. Mechanical strain, or changes of the form of the base-metal, invariably cause, sooner or later, them to peel away from the surface. This behaviour is due to the following causes:

1. All technical coatings—whether produced with or without the use of intermediaries—are bound to the base only by very weak surface forces (friction, adhesion, residual valencies of the crystal lattices). Between the coating and the metal there always exists a region of inhomogeneity. The strength of adhesion is therefore small in comparison with the mechanical strength of the polycrystalline structures of the pure metals forming the base and the coating.

2. It is practically impossible to use materials for coating with the same modulus and limit of elasticity, as the base metal and the same limiting values for stretch and break in a static experiment, as well as identical thermal properties. Therefore, even small mechanical stresses or changes of temperature applied to the metal are liable to cause the coating to peel away from the base.

3. Most of the coatings produced technically retain some faults due to the process of their formation. Galvanic deposits contain inclusions of hydrogen and weak places in the texture. They consist of particles

of variable size and exhibit local chemical changes due to the influence of the liquid in the bath and capillary inclusions of this liquid. In spray-coatings, there are always microscopic cavities and pores. The whole coating has the structure of a heap of sand. These pores are weak places in the texture. All these faults facilitate the splitting-off of the film from the base metal under the influence of mechanical forces or corrosion.

4. Galvanic couples are formed at cross-sections of metallic pieces coated with a metal deposit as soon as moisture has access to the contacts between the two metals. In this way an electrochemical corrosion and destruction of one of the metals is made possible and ultimately leads to a separation of the coating from the base.

5. The splitting-off of the coatings is further promoted by insufficient cleaning of grease and dirt from the base before coating; by roughening of its surface by scouring or sand-spraying and—if intermediary layers are used—by incompleteness of these layers.

6. When pieces of irregular shape are coated by spraying, different surfaces are liable to obtain coatings of different thickness, possessing, therefore, different properties.

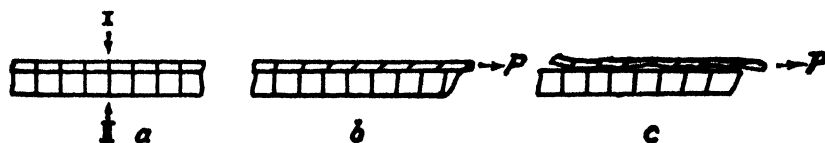


FIG. 1.—I. Metallic coating. II. Ground-metal. Diagrammatic representation of the destruction of coated metal pieces by mechanical forces.

(a) Before stress. (b) Deformation and structural change (*Verfestigung*) under the influence of the compressing, stretching and twisting field of force P , which changes the form of the coating more than that of the ground-metal. (c) The form-change of the ground-metal lags behind that of the coating; the latter ultimately splits off.

These six points are deduced from the recent work of a great number of investigators. The descriptions of the practical deficiencies of coated metallic pieces which repeatedly occur in all the papers give full support to the statement, that *all material prepared by the galvanic method or by spraying, can be submitted mostly to very weak mechanical or chemical forces.*

Starting from the exact knowledge of the above discussed faults we have tried to produce coatings of higher resistance. The essential considerations are the following: So long as the base metal is reversibly strained (within its elastic limits), by repeated change from a maximum to a minimum load, all coatings with a thickness of up to 0.1 mm. obey Hook's law, *i.e.*, after releasing the strain they return to their original form together with the base-metal, and therefore do not split off. The coated material behaves in the same way as the pure metal of the base and of the coating separately.

But when, after a strong or often repeated stress, the elastic limit of the base-metal or of the coating is exceeded and appreciable permanent stretch remains after releasing the strain, tension must occur between coating and base and ultimately produce a splitting of the coating from the base.

Such tensions occurred equally if the strain was purely mechanical at room temperature (as diagrammatically shown in Fig. 1), or was due

to compressing, stretching and twisting generated by inhomogeneous thermal expansion, as in Fig. 2.

These evident defects of the mechanical behaviour of coated materials as compared with homogeneous metals obviously call for improvement. The technique of galvanisation and metal-spraying has already obtained some results in this direction. By selecting for the coatings appropriate materials with mechanical properties (in the elastic and the plastic region) as near as possible to those of the base-metal, it was

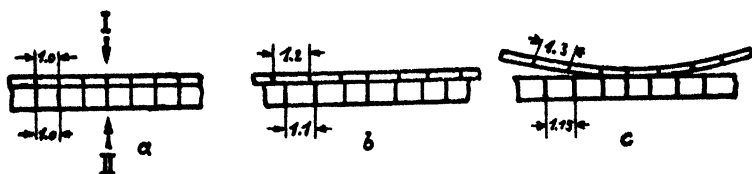


FIG. 2.—I. Metallic coating. II. Ground-metal. Diagrammatic representation of the deformation produced by heating coated metal pieces.

(a) Before heating. (b) Inhomogeneous thermal expansion of coating and base metal. The adhesive forces are at this stage stronger than the tensions due to expansion and splitting-off does not yet occur. (c) The piece has been heated to a higher temperature; the difference between the thermal expansions of the coating and of the base metal has become too great, and the coating is split off from the base.

possible to diminish to a certain degree the destructive effects of change of shape. Another possibility is offered by "bridging" the gap between the properties of the coating and those of the metal by intermediary layers with properties lying midway between them. However, the results obtained so far by both of these methods have, in the long run, not been satisfactory.

Our experiments have shown that better results can be obtained by combining metal-sprays with varnishes of high plasticity. The use

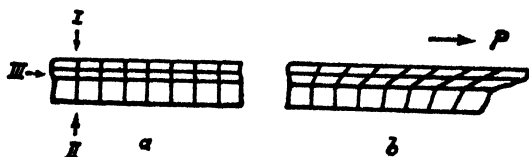


FIG. 3.—I. Metallic coating. II. Ground-metal. III. Varnish-layer. The effect of mechanic strain on metallic coatings buffered by an intermediate layer of varnish. a. Before strain. b. Change of shape and buffering action of the varnish. If the varnish layer does not follow the deformation of the coating as well as that of the base-metal, the coating would have split off from the metal.

of these materials was suggested by the fact that certain soft varnishes has for instance linseed-oil copal varnish, or bakelite varnish—are highly plastic and therefore able to stand great changes in shape. If a way could be found to introduce such varnishes as intermediary materials into the texture of sprayed metallic coatings, they must enable a certain "equalisation" of mechanical properties of coating and ground-metal. The varnish-layer would serve as a kind of "buffer" between them. This desired rôle of the varnish layer is illustrated in Figs. 3 and 4, which correspond to Figs. 1 and 2 for the case of ordinary sprayings.

Experiments have shown that intermediate layers of varnish in fact show the expected buffering properties.

The following experiments have been made with sheets of hard brass covered with sprayed nickel. Hard brass has been chosen in view of its high elasticity, as compared with that of soft annealed brass. Nickel has been selected for the known rough-grained structure of its spray-deposits. One may easily recognise this property of nickel by comparing Fig. 5* (sprayed nickel-coating) with Fig. 6† (sprayed zinc, as an example of a metal with finer grains).

It is well known empirically that coatings of coarse-grained structure, deposited on highly elastic base-metal, split off much more readily than coatings of finer grain formed on less elastic bases. On the other hand, coatings possessing larger grains, and therefore larger pores, are more suitable for introduction of intermediate substances than fine-grained deposits with less space between the single particles.

Previous investigations by the author¹ have shown that coatings produced by spraying are micro-porous masses of single grains. It was therefore expected that a sufficiently thin liquid varnish would be able to enter the capillaries between the particles—in the same way as has been observed by the author² with other liquids. On drying,

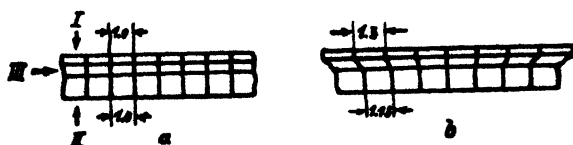


FIG. 4.—I. Metallic coating. II. Ground-metal. III. Varnish-layer. The thermal changes of coated metal-pieces buffered by an intermediate layer of varnish.

a. Before heating. b. Deformation due to heating and the buffering effect of the varnish-layer between the two metals with different coefficients of expansion. If the layer does not adjust its shape equally well to the changed shape of the coating and of the base metal the coating would split off.

the varnish should form an efficient cement, filling up the cavities between the grains and tightly joining them together. With ordinary spray-coatings the sprayed metal does not adhere closely to the base metal; thus the varnish can be expected to fill up the free spaces left between the two metals and cement them together, just as it joins the single grains of the coating.² The conditions prevailing in the case of coatings without varnish are shown in Fig. 7†; the example is that of tin on an aluminium sheet.

The possibility of closing microscopic capillaries between the grains of a metallic coating by introduction of an adhesive substance has already been shown by observation of the changes occurring with fresh zinc coatings on iron.³ At first the air freely circulates in the open pores; moisture and carbon dioxide contained in the air react with zinc forming hydroxide and basic carbonate. These products being

* Plate LXVI.

† Plate LXVII.

¹ Reininger, H., *Z. Metallh.*, 1933, **25**, 42-44, 71-73 and 286-287; *D. Metallw. Ind. u. Galvanotechn.*, 1933, **31**, 89-90, 110-112, 130-131, 174-175, 194-196 and 213-214; *Hauszeitschr. Aluminium d. V.A.W. u. d. Erftwerf A.-G.*, 1931, **3**, 66-75.

² Reininger, H., *D. Metallw. Ind. u. Galvanotechn.*, 1934, **32**, 235-236.

practically insoluble, form a kind of cement which ultimately closes the capillaries. After this stage has been attained the structure of the zinc coating becomes so close that the air no longer has access to the iron and the latter is efficiently protected from rusting.*

The firmer adhesion and greater resistivity against changes in shape which can be expected from varnished coatings is illustrated by Figs. 8 and 9; the former shows a sprayed structure without filling material, with microscopic cavities and an incomplete adhesion between coating and base; the latter a structure with varnish filling the pores, and ensuring complete contact with the base.

The experiments we have performed already provide a proof of the superiority of combined metal-varnish coatings to the old non-filled metallic sprays.

We made a micro-metallographical study of 108 unvarnished metallic coatings and compared them with 122 varnished samples at different magnifications (10, 100, 300, 500, 1000 and 2000). The following interesting facts have been observed: The ordinary unvarnished coatings representing always more or less loose masses of single metallic grains,² sections showing their real, undistorted structure can be obtained only with the greatest care. Very slow hand-grinding is necessary to get satis-

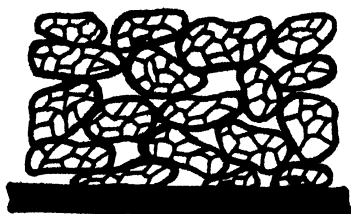


FIG. 8.—The structure of an ordinary sprayed coating consisting of single grains with microscopic pores between them.



FIG. 9.—The capillary cavities seen in Fig. 8 are filled up with varnish.

factorily clear results. In machine-made sections the real structure is more or less destroyed by the tearing out of single particles and by plastic deformation (flattening, smoothing) of the regions which have been in contact with the grinding and polishing discs. The true porosity existing in the texture and due to the process of its formation by spraying is masked by grinding—whether by hand or by machine—the protruding grains being plastically deformed and pressed into the adjoining cavities.

In sections made from *varnished* samples, the actual shape and size of the cavities existing in the original structure can readily be recognised because the filling with varnish prevents their destruction.

This behaviour of varnished and unvarnished coatings leads to the possibility of certain deceptive results. The structure shown in Fig. 10 appears close, but it is, in truth, coarse and is rendered close only

* This protective action of sprayed zinc coatings has opened the way to quite unexpected possibilities. In tropical countries, with their sudden changes from dry to moist conditions, only bronze window frames have been considered as able to stand prolonged use; to-day they can all be replaced by the much cheaper cast-iron frames, efficiently protected from rusting by a coating of sprayed zinc.

superficially by the influence of grinding; on the other hand, the varnish-filled structure shown in Fig. 12* appears at first glance to be coarse, but is in truth efficiently tightened by the varnish filling the capillary cavities, and is correspondingly firm. The varnish, which has entered the capillary hollows and dried there, prevents the deformation of the single spray-grains and their pressing into the pores during the grinding, which was possible as long as the grains were separated by empty spaces, as appears from Figs. 10* and 11.

Fig. 13† shows a strip of brass sheet, 150 mm. long, 21 mm. wide, 0.5 mm. thick, to which, after the usual roughening with a sand-blower, has been given a coating of sprayed nickel of about 0.1 mm. thickness. The structure of the coating is that shown in Fig. 10. A single bending of the sheet into the form shown in Fig. 13 caused a complete splitting-off of the coating; this result confirms the previous observations made by the author,¹ showing the weakness of sprayed metal coatings. Figs. 13-15‡ show that the coating has not simply cracked, but really peeled off from the base metal in large flakes.

Unlike the samples shown in Figs. 13-15 the samples used in Figs. 16-18,§ after having been covered by spraying with 0.1 mm. of nickel have been saturated with a soft copal-varnish. Their structure must be that shown in Fig. 12. After 3 days' drying in the air the samples have been bent in the same way as in Fig. 13; there were no fissures, much less any splitting-off from the ground metal.

Small fissures normal to the direction of the strongest stress and caused by exceeding the limit of the stress-resistance of the coating appear first after the metal strip has been bent through an angle of 180° (as shown in Fig. 19).§ Even at this stage the adhesion of the coating to the base was not yet broken, but the stress-resistance of the coating failed at the region of highest strain. The coating, therefore, does not flake off; it only cracks because its plasticity is smaller than that of the brass base, which can be bent through this angle without breaking.

To make this point clear we reproduce in Fig. 20§ the photograph of a nickel-coated strip, which has not been impregnated with varnish (structure as in Figs. 10 and 13-15), as it appears after the same treatment (bending through 180°). In addition to cracks due, as above, to the limited plasticity of the coating, we recognise a flaking-off of large sections of the coating. Thus, not only the limit of plasticity of the coating, but also the limit of its adhesion to the base have been exceeded by bending.

In order to obtain some data concerning the plastic properties of the coatings we made stretching experiments with brass sheets 0.5 mm. thick, coated on both sides with 0.1 mm. of nickel. The strips were 150

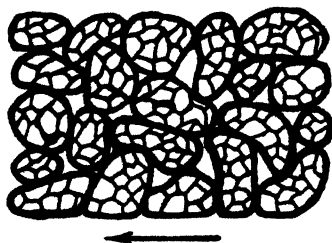


FIG. 11.—Diagrammatic picture of the formation of an apparently tight structure, like that shown in Fig. 10. The single particles of the sprayed metal are pressed together by the grinding and polishing instruments in preparing the sample for micro-metallographical inspection. Further away from the region affected by grinding the original porous structure persists.

* Plate LXVIII.

† Plate LXIX.

‡ Plate LXX.

§ Plate LXXI.

mm. long and 21 mm. wide; the test length was 100 mm. (Figs. 22a * and 23a).† The experimental arrangement is shown in Fig. 21.‡

The plasticity of the coatings can be characterised by the elongation of the test length at which the coatings first crack or split off. The bending experiments, described above, have already shown that the destruction of the coatings in all cases begins well before that of the brass base. (The limiting value for the stretching of the brass sheets lies at about 12 per cent. elongation, corresponding to a force of about 30 kg. per sq. mm. on the breaking surface.)

Up to an elongation of about 5 per cent. all coatings—varnished and unvarnished—remain intact (Figs. 22b and 23b). At elongations greater than 5 per cent. all samples begin to show scars and dislocations (Figs. 22c and 23c); at higher elongations, but nevertheless well before the strip is torn in two, cracks appear in the coatings and single flakes begin to split off. Varnished and unvarnished coatings behave in the same way, but the appearance of the flakes is different, the unvarnished coatings falling off in a great number of small scales (Figs. 22d), and the varnished coatings in large single pieces.

Stretching experiments—unlike the bending experiments described above—do not prove that varnished coatings adhere more effectively than ordinary ones. Since greater elasticity and firmer adhesion of the former follow from the results of the bending tests, the failure of the varnished coatings in stretching experiments calls for some explanation. We can explain it as a typical inter-surface phenomenon in the following way.

During stretching, each single grain is obstructed in its deformation by the adjoining grains. The situation is essentially the same as that occurring when all kinds of polycrystalline agglomerations (as distinct from single crystals) are subjected to deformation. The mutual obstruction of single grains in the coating leads to the same unfavourable conditions of stretching as those which prevail, for instance, in the polycrystalline structure of brass sheet. With growing plastic deformation, the mutual obstruction of the grains becomes stronger and the internal tensions due to the pressure they exercise on each other, and the resulting bending of the single particles, increase more and more. The deformations and tensions to which single grains are submitted ultimately overcome the adhesion, and the coatings split off the base. This explanation involves the assumption that the cohesion of the base metal and of the coating, taken alone in the normal and in the deformed state, are greater than the adhesion between the two, an assumption which is correct in practically all cases, because neither the varnished nor the unvarnished coatings can ever stick to the ground metal with a cohesion equivalent to that of the homogeneous metal itself.

This explanation affords an easy understanding of the fact that no difference between the two kinds of coatings is observed in the stretching test. The forces separating the coating from the base in both cases exceed the critical values of adhesion, despite the difference which exists in the strength of the deformed coatings. The fact that the adhesion is much firmer in the case of varnished coatings remains well established by the bending experiments (Figs. 13-20).

A further demonstration of the different strength of adhesion can be given by gradually grinding the coating off the base. We prepared about 20 horizontal sections of diminishing thicknesses, from both kinds of

* Plate LXXIII.

† Plate LXXIV.

‡ Plate LXXII.

coatings. The result of their examination was : In the process of grinding, single particles are torn out from the structure of non-varnished coatings ; the surface of the sections is correspondingly rough ; the relatively large chips do not adhere to the emery cloth, which remains clean. Fig. 24 * shows the surface of such a section.

The behaviour of varnished coatings is very different. Their surface remains smooth and clean ; no tearing out of macroscopic grains can be observed in the course of grinding. After a certain time the emery-cloth becomes smeary ; the whole grinding process can be described as "smearing." Fig. 25 * illustrates the characteristic appearance of a section of this kind.

The characteristic differences observed in the above experiments can easily be explained. A roughening of the surface, with tearing off of macroscopic chips, occurs in all cases in which the single particles composing the structure are not firmly enough bound together. If this is the case, the surface must remain more or less rough despite all grinding, and the microscopic examination reveals (as in Fig. 24), in addition to bright metallic grains, dark patches corresponding to the holes left by the grains which have been torn out.

In a structure impregnated with varnish the single particles are so firmly bound together by the varnish (which softens under the influence of grinding) that they cannot be torn out from the surface. They are, instead, "smeared over," that is to say, pressed flat into the varnish ground in which they are embedded. The surface therefore remains coherent and smooth, free from the holes and cavities which are conspicuous in Fig. 24. (The darker patches in Fig. 25 are not holes, but sections of the varnish-layers in which the metal grains are embedded.)

It is further to be remarked that when unvarnished coatings are ground nearly down to the base the tensions produced by grinding in the structure cause the last thin film of the coating to split off the base, as is shown in Fig. 26.† The varnished coatings, on the contrary, can be ground down until only a last layer of grains remains on the base without any splitting off from the base metal. In Fig. 27 † the base plate is slightly visible through the last remnants of the varnished coating.

The comparison of Figs. 26 and 27 forms a further convincing proof of the considerably firmer adhesion of the varnished as compared with ordinary coatings.

We have so far discussed the *mechanical* properties of the new coatings, using the experimental data available up to the present. We must now consider the *chemical* behaviour of varnished coatings.

It seems unnecessary to explain that organic solvents (alcohols, acetone, turpentine, linseed oil, etc.) destroy the varnish-layers. It is therefore impossible effectively to protect the coatings and the base material from the influence of such substances by using the new coatings. After having destroyed the varnish, the solvent finds its way into the capillaries and penetrates to the base-plate.

Good resistivity has been observed with varnished coatings exposed to water, salt- and acid-solutions, or placed in damp rooms. This satisfactory behaviour is easily understood, since the varnish-layers, unsoluble in these chemicals, close the capillaries of the coatings to them and do not permit contact either with the base plate or with the metal grains of the coatings ; both are thus effectively protected against

* Plate LXXV.

† Plate LXXVI.

corrosion. Electrochemical corrosion due to formation of galvanic couples at the boundary between base metal and coating³ is also made impossible by the varnish which forms an insulating layer between them.

Further Experiments Started or Planned.

We have started experiments to test the resistance of the varnished coatings to corrosion by different agents over longer time intervals.

It has been found empirically that varnishes are not all equally suitable for impregnation; therefore further experiments are desirable to find out the best ones and their most appropriate concentrations. Especially needed are experiments on the changes of structure of the varnished coatings when in longer use (change of elasticity and other possible phenomena of ageing). Such experiments must form a necessary part of a general durability-test of coated pieces. The phenomena of fatigue, the resistance to prolonged or periodical mechanical strain must be investigated too. The measurements of the static properties (resistance to pressure, stretching, bending, shearing and chipping, strength of adhesion to the base) must be measured more in detail, with coated pieces as well as with coatings alone. It is necessary to determine the most appropriate thicknesses of the coatings and their influence on the properties of the coated pieces. The experiments must be extended to different metals (different bases as well as different coating materials). Only after such detailed experimental results are available shall we be in a position definitely to assess the practical usefulness of the varnished coatings; in some special cases their great value has already been established.

Summary.

The mechanical properties of ordinary sprayed coatings have been compared with those of the same coatings after impregnation with varnishes. Sheets of hard brass covered with nickel have been used for the tests. In the following points satisfactory results have been obtained and the varnished coatings proved to be superior to the ordinary ones.

1. Soft copal varnishes and bakelite varnishes—when used in appropriate dilution—penetrate into the porous structure of the sprayed metal coatings and, after drying, form intermediary layers between the metal grains.
2. These layers cement the metal grains together and to the base plate; in this way the coatings become stronger and their adhesion to the base metal firmer.
3. Metal pieces having varnished coatings can be deformed plastically to a higher degree than those with ordinary coatings, without the surface-film splitting off the base.
4. It is possible to grind the varnished coatings practically down to the base. The strong mechanical tensions caused by grinding do not lead to a splitting-off of the coating.
5. The varnished coatings do not form galvanic elements with the base metal and are therefore not liable to electrochemical corrosion. The resistance to corrosion is higher in the case of varnished than in the case of unvarnished coatings.

Explanations have been sought for all the effects observed; new experiments have been suggested which are necessary in order definitely to establish the practical value of the new method.

³ Evans, U. R., *The Corrosion of Metals*. Edward Arnold, London, 1924.

FACTORS INFLUENCING THE FORMATION AND STRUCTURE OF HOT-DIPPED TIN COATINGS.

BY EDWARD J. DANIELS, M.Sc.

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The present paper describes recent, hitherto unpublished work relating to the conditions of formation of hot-dipped tin coatings, and provides a critical review of the present position of the subject.

The tinning or soldering of steel or copper consists in bringing the solid metal in contact with the liquid metal in the presence of a "flux," followed by cooling to room temperature.* It is essential that wetting should occur, and much has been published on the influence of surface tension and fluxing on this phenomenon, particularly as regards soldering.

Crow¹ considers that the flux acts merely in a chemical capacity, that is to say, cleans the surfaces and produces a wetting condition. According to Desch² the function of the flux is mainly to remove surface films of oxide and other foreign matter which prevent wetting. Dean³ suggests that at the temperature of soldering, fluxes give up hydrogen chloride, which replaces the adsorbed air on the metal surface and is subsequently replaced by the solder. A more detailed mechanism of fluxing, involving chemical reaction between flux and the basis metal, followed by further reaction of the products with the coating metal has been proposed by Daniels.⁴

The efficiency of halide fluxes in promoting the flow of solder on copper was demonstrated in an investigation carried out by Dean and Wilson.⁵ The greatest spread was obtained with stannous bromide; followed by hydrogen bromide, dry hydrogen chloride, stannous chloride, ammonium chloride, ammonium bromide, zinc chloride, etc. Coffman and Parr⁶ confirm the increased spreading given by stannous chloride, zinc chloride, hydrogen chloride, and ammonium chloride compared with rosin. They also found that hydrogen chloride decreased the surface tension of solders compared with that observed *in vacuo*. They suggest that the most important function of the flux is to lower the surface tension of the liquid metal. The view that surface tension is the governing factor in soldering is emphasised by Libman.⁷

Harkins and Feldman⁸ have developed a relation between spreading coefficient (S), work of adhesion (W_a) and surface tension (W_c);

* For the technical side of hot-dipping in tin, zinc, lead, etc., see H. S. Rawdon, "Protective Metallic Coatings," New York, 1928.

¹ T. B. Crow, *Trans. Faraday Soc.*, 1924, 20, 199.

² C. H. Desch, *Trans. Faraday Soc.*, 1924, 20, 118.

³ R. S. Dean, *Theoretical Metallurgy*, 1924, 150.

⁴ E. J. Daniels, *J. Inst. Metals*, 1932, 49, 169.

⁵ R. S. Dean and R. V. Wilson, *Ind. Eng. Chem.*, 1927, 19, 1312.

⁶ R. W. Coffman and S. W. Parr, *Ind. Eng. Chem.*, 1927, 19, 1308.

⁷ E. E. Libman, *Univ. Illinois Eng. Expt. Stn. Bull.* No. 173, 1928.

⁸ W. D. Harkins and A. Feldman, *J. Amer. Chem. Soc.*, 1922, 44, 2665.

$S = W_s - W_a$, and have shown its validity for the spreading of one liquid on another. It is difficult to apply to solids since it is difficult to determine their surface tensions.

The study of the flow of liquids and solids on liquid surfaces, and of the structures of the films produced has been pursued for many years.⁹ Devaux,¹⁰ from a study of the wetting of solid surfaces and the effect of surface films on the solid, has concluded that "wettability" is a property essentially localised in an unique layer of molecules, the most superficial layer of the body. He considers that the adherence of liquids to solids is of the molecular order and disappears as soon as there is no longer direct contact of the molecules. Crow (*loc. cit.*) suggests that whenever wetting of one metal by another occurs, alloying invariably follows and also that whenever alloying occurs it must have been preceded by wetting.

The Wetting of Solid Metals by Liquid Metals.

Although cleaning and fluxing precede soldering or tinning, etc., it is more convenient to consider first the formation of a film of liquid metal on a solid, assuming that the metal surfaces are perfectly clean. The usual expression * relating the stability of a drop on a solid surface to the relative magnitudes of surface tension of solid, liquid and interface does not lead very far since it contains two unknowns. The equation of Harkins and Feldman given above seems more likely to be of assistance as it contains only one unknown, W_a , the work of adhesion between solid and liquid. In the argument which follows it is proposed to consider this adhesion from the molecular standpoint, in order to attempt to obtain a more easily understood picture of the forces determining wetting.

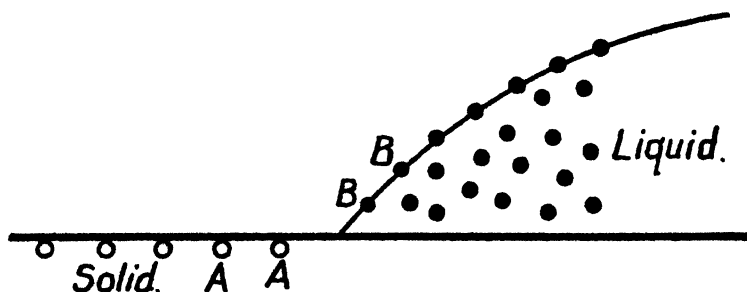


FIG. 1.

Fig. 1 is a diagrammatic representation of a drop of molten metal, say tin, resting on a solid metal, say iron. Since both metals are assumed to be perfectly clean the atoms *A* on the iron surface will possess some unsatisfied affinity, as will the atoms *B* of the tin surface. If these affinities can in some measure satisfy each other, the projections which are constantly appearing on the edge of the tin drop due to thermal agitation will be fixed by linkage to the iron atoms, so that the boundary of the drop will move over the solid. The strength of the linkage will naturally vary with different pairs of metals.

Large quantities of tin are applied industrially as a coating to both steel and copper. Tin forms intermetallic compounds with iron and

⁹ N. K. Adam, *The Physics and Chemistry of Surfaces*; E. K. Rideal, *Surface Chemistry*.

¹⁰ H. Devaux, *J. Phys. et Radium*, 1923, 4, 293.

* See, for example, Crow, *loc. cit.*, p. 200.

copper, and as a result of this tendency to combine, the coatings on tin-plate and tinned copper consist of a layer of pure tin, separated from the basis metal by a more or less well-developed layer of alloy. The thickness of the alloy layer varies considerably with the nature of the metals involved; for tin on steel, an oblique section through the coating and a magnification of about 1000 are usually necessary for microscopical observation.

In the commonest cases of wetting of a solid metal by a liquid metal, it appears that the tendency to form an intermetallic compound is a factor in overcoming the cohesion of the liquid metal. It is significant that iron, copper and nickel combine with tin, zinc and antimony, respectively,¹¹ and that they are wetted by these metals. Iron can also be coated with aluminium, with which it forms a compound.¹² In the case of iron and cadmium or lead there is strong evidence that combination occurs,⁴ and iron is wetted by both these metals. It must not be concluded, however, that intermetallic compounds must be formed between the solid and liquid metals if wetting is to be possible. The ability to form a solid solution is probably also a factor; for instance, silver can be coated with bismuth, although intermetallic compounds are not formed in the system silver-bismuth.¹¹

On the basis of the above views, if the metal pair form neither solid solutions nor compounds, the tendency to wetting should be relatively small. Thus attempts to coat copper with bismuth have failed, although a coating can easily be produced if 1 per cent. of tin is added to the bismuth.

The Interfacial Alloy.

The formation and growth of alloys between pairs of metals when one or both is solid, has been studied by a number of workers, and it has been shown that the process is governed by diffusion.^{13, 13, 14} According to Jeffries,¹⁵ reactions in solid metals may be governed by availability of atoms rather than by the stability of the resulting compound. As a result, the alloy layer may be duplex,¹⁴ or may be of molecular thickness only.¹⁶ In general, the time taken to produce a hot-dipped coating is insufficient for the concentration of the liquid metal at the solid surface to fall so low that a second alloy layer begins to form.

The nature of the interfacial alloy formed between molten tin and solid copper is uncertain. According to Crow,¹⁷ at relatively low temperatures (237°-239° C.) tin-lead solder attacks copper forming the compound Cu₃Sn. At intermediate temperatures (325°-360° C.) a very thin band of Cu₃Sn makes its appearance between the CuSn and the copper, whilst at high temperatures (402°-497° C.) Cu₃Sn layer is thicker than the CuSn layer. This compound CuSn—or more accurately Cu₃Sn,^{18, 19}—is also formed by the action of pure tin on solid copper below 300° C. In the present paper the interfacial alloy will be denoted by "CuSn," without discussing its composition further.

The "CuSn" layer does not thicken with time, as it is being attacked continually by the tin. This attack appears to take place along grooves, resulting in the loosening of blocks of compound which enter the "pure" tin portion of the coating.

¹¹ Anon, *International Critical Tables*, Vol. II.

¹² C. H. Desch, *Report on Diffusion in Solids*, British Association, 1912.

¹³ J. Weiss, *Rev. Met.*, 1924, **21**, 18.

¹⁴ G. Tammann and H. J. Rocha, *Z. anorg. Chem.*, 1931, **199**, 289.

¹⁵ Z. Jeffries, *Trans. Amer. Inst. Min. Met. Eng.*, 1924, **70**, 311.

¹⁶ W. Hume-Rothery, *J. Inst. Metals*, 1927, **38**, 127.

¹⁷ T. B. Crow, *J. Inst. Metals*, 1926, **35**, 61.

¹⁸ J. D. Bernal, *Nature*, 1928, **122**, 54.

¹⁹ M. Hamasumi, *Kinoshu no Kenkyu*, 1933, **10**, (4), 137-147; *Inst. Metals Abs.*, 1933, **53**, 550.

The crystal structure of the alloy layer formed in hot-dipping is difficult to determine microscopically, since the layer is generally extremely thin and is not etched by the usual methods. When tinned copper is treated with a boiling solution of sodium plumbite, the outer tin layer is dissolved away, leaving the alloy layer exposed. Microscopical examination of the alloy surface shows it to be covered with innumerable tiny peaks of compound, which are, of course, also readily seen in cross-section (Fig. 2).^{*} Such a highly irregular surface is useless for micro-examination and the alloy is too thin to allow of polishing and etching. In the case of tinned steel the irregularities in the surface of the compound layer, consisting of FeSn_3 , form a distinct pattern easily seen with the naked eye. This pattern or "mottle," which is illustrated in Fig. 3,^{*} has been discussed by Hoare.^{20, 21} Traces of a similar structure may sometimes be observed on tinned copper after stripping in plumbite followed by etching in ferric chloride.

The Effect of Other Metals on Interfacial Alloys.

The preceding discussion refers to pure metals, but in practice alloys are often coated, and other metals may be added to the liquid, so that from the scientific and technical viewpoints it is desirable to know how the presence of a third metal affects the normal alloy layer.

Examination of the somewhat scanty data available shows that additions may have very varied effects. Lead added to tin, for example, does not affect the composition or structure of the interfacial compound¹⁷ and reduces attack on copper merely by dilution of the active tin.²² It may happen in other systems, however, that the addition of a metal, which by itself is inert, to the molten metal gives rise to enhanced attack. This is the case for additions of cadmium to zinc²³ in the coating of steel. Further, although molten cadmium and lead are individually inactive towards mild steel,⁴ fluxed steel is vigorously attacked by molten cadmium containing 12 per cent. of lead and by molten lead containing 12 per cent. of cadmium. It is interesting to note that attack by these alloys pits the steel surface distinctly, whilst even greater attack by pure zinc at, say, 450° C., leaves the steel surface quite smooth. A tendency to such pitting has been observed in the action on steel of zinc containing aluminium.

The majority of steel which is tinned is free from alloy additions, as is the tin used, so that, as far as the writer is aware, no work has been done on the effect of a third metal on the FeSn_3 layer. The presence of isolated dross crystals in the tin layer in tinplate has been shown by Hoare.^{20, 21}

The reaction between tin and copper affords an example where additions to both solid and liquid metals act differently from those discussed above. Hartley²⁴ found that in the course of a prolonged attack by tin at 300° C. upon alpha- and beta-brasses a brittle substance formed at the surface of the brass. This white alloy contained approximately copper 43, zinc 45, and tin 12 per cent., and he suggested as a result of an X-ray examination by Bradley that it was a solid solution of the two intermetallic compounds Cu_2Zn_3 and Cu_3Sn . The alloy formed when tin attacks copper containing 8 per cent. of aluminium was found by the writer⁴ to contain tin 46.4, copper 49.0 and aluminium 3.9 per cent., which indicated that it was a solid solution of tin and aluminium in Cu_3Sn . Both Hartley and the writer produced the alloys at temperatures at which,

^{*} Plate LXXVII.

²⁰ W. E. Hoare, *J. Iron and Steel Inst.*, 1934, 129, 253-264.

²¹ W. E. Hoare, *Swansea Tech. Coll. Met. Soc.*, 15th Dec., 1934.

²² S. J. Nightingale, *British Non-Ferrous Metals Research Assn. Report, Assoc. Series No. C234-214*, Dec. 1929, p. 61.

²³ E. J. Daniels, *J. Inst. Metals*, 1931, 46, 81-96.

²⁴ H. J. Hartley, *J. Inst. Metals*, 1927, 37, 196.

according to Crow,¹⁷ compounds richer in copper than "CuSn" are formed, which would account for Cu_3Sn and Cu_5Sn being found in them.

The behaviour of tin coatings on copper alloys, particularly those containing nickel, indicates that additions to the solid may result in a broken-up alloy layer. This is being investigated.

Of additions to the molten tin only antimony has yet been studied in any detail. Nightingale²² found that 4 per cent. of antimony in the tin considerably reduced its corrosive action on copper. In order to elucidate this, experiments have been carried out in which copper was heated in tin containing up to 50 per cent. of antimony and the cross-section of the solidified mass examined microscopically.

Melt No. 1.—SnSb on copper. Interfacial alloy purple in colour (Cu_3Sb).

Melt. No. 2.—Sn + 5.85 per cent. Sb on copper. Alloy layer very thin even after five minutes, but definitely purple (Cu_3Sb).

Melt No. 3.—Sn + 1.46 per cent. Sb on copper. Same as No. 2 (Cu_3Sb).

Melt No. 4.—Sb on copper. Wide purple alloy band (Cu_3Sb).

Melt No. 5.—Sn on copper. Very thin white alloy band ("CuSn").

From these observations it appears that the antimony addition acts by forming Cu_3Sb , not "CuSn," and since the percentage of antimony in Nightingale's experiments was small the attack could only be small. A very thin white fringe was observed between purple compound and tin in melt No. 3, suggesting that the copper antimony compound was being changed into a tin compound—probably "CuSn." A thin slab of Cu_3Sb was found to tin quite readily when dipped in molten tin after fluxing, and when allowed to remain in the tin for a few minutes it became surrounded by a similar fringe of white compound. In any case, when the purple alloy layer becomes detached from the copper, reaction with the tin soon changes it into "CuSn"²³ so that the free compound in the tin-antimony bath appears just as if antimony was absent.

Fluxing.

After a preliminary cleaning, which generally consists of degreasing and pickling and which it is not proposed to discuss here, the work is "fluxed" immediately before being dipped into the bath of molten metal. The flux may be applied as a concentrated solution or may be used as a liquid cover to the molten metal.

It is a matter of general observation that in soldering or hot-dipping the flux must be molten at the working temperature. Nightingale (*loc. cit.*, p. 53) has emphasised this in connection with the use of zinc chloride for soldering at temperatures below 260° C. He found that the eutectic mixture of zinc chloride and ammonium chloride, which melts at 179° C., can be used satisfactorily at temperatures approaching the tin-lead eutectic point when "killed spirits" gave joints full of flux inclusions. In the "tinning" of copper by dipping in the tin-lead eutectic, continuous coatings have been obtained at temperatures as low as 188° C., using the eutectic flux (1 part NH_4Cl ; 3 parts ZnCl_2); when $\text{ZnCl}_2 \cdot 2\text{NH}_4\text{Cl}$ was the flux, a continuous coating could not be obtained below 320° C., and stannic bromide was useless even up to 340° C., probably owing to the formation of lead bromide.

For applying coatings of pure tin to copper, the bath must be maintained at temperatures approaching 300° C., when using "killed spirits" or $\text{ZnCl}_2 \cdot 2\text{NH}_4\text{Cl}$ as flux. With the latter compound bare spots are always obtained below 280° C., the flux sticking to the copper as a solid

²³ W. Bonsack, *Z. Metallkunde*, 1927, 19, 107-110.

coating which prevents tinning. Since it is possible that minute bare patches caused by solid flux may be one of the sources of porosity, it was decided to attempt to find a flux which would be molten below the melting-point of tin. The salt most suitable for this purpose is stannic bromide, which melts at $31^{\circ}\text{C}.$, and is extremely fluid at all tinning temperatures.

Tests made with this flux showed it to be quite satisfactory for tin and tin alloys (excepting *tin-lead*) at all temperatures. The flux was made in the laboratory by allowing bromine to drop into a vessel containing granulated tin covered with a layer of water, and filtering off the black residue. The concentrated solution so obtained was applied to the copper surface and the specimens heated to about $200^{\circ}\text{C}.$ before immersion in the tin bath. In this way a continuous coating could be obtained at $240^{\circ}\text{C}.$, with a dipping time of only one second, on a specimen $2 \times 7 \times 0.05\text{ cm.}$, showing that the flux possesses the desired fluidity.

In addition to possessing fluidity, a flux for use in hot-dipping must conform to certain chemical requirements. This question has been discussed elsewhere,⁴ where a detailed mechanism of the fluxing process has been described. It does not appear necessary for the flux to lower the surface tension of the liquid metal, as has frequently been claimed.

Hydrogen is capable of reducing tin oxide and copper oxide at temperatures below $300^{\circ}\text{C}.$, and it has been found possible to coat copper wire by immersion in tin in an atmosphere of hydrogen. The tin and the copper surfaces are cleaned by the hydrogen which is thus a true "flux."

Steel cleaned with emery can be tinned by dipping in tin containing a small amount (0.05 per cent.) of phosphorus. Tin containing this amount of phosphorus will also partially coat copper, without any other flux being used. There is no doubt that the surface of the steel after cleaning with emery paper is still slightly oxidised, and it is probable that the phosphorus in the molten metal removes the oxygen as a volatile compound (P_2O_5 sublimes at $250^{\circ}\text{C}.$) and so enables perfectly clean steel to come into contact with the coating metal.

The Solidification of the Coating.

When the sheet of metal has been cleaned, fluxed and dipped in the tin bath for a suitable length of time, it is withdrawn and cooled. On leaving the dipping bath the work is covered with a layer of alloy, which is in turn covered by a layer of molten tin, which is being cooled from the outside and drained under the influence of gravity or by mechanical shaking.

The thickness of the liquid layer depends on its composition and the temperature of dipping, which control the fluidity.* If the process has been carried out correctly the liquid coating will be smooth, and it is desirable that it should remain so until it has set. On the other hand, the coating may become "rippled," the tin accumulating in ridges, where it solidifies, leaving the rest of the surface very thinly covered.

If another metal is added to the tin, to produce an alloy having certain characteristics, smooth coatings can be obtained. For example, tin containing as little as 0.04 per cent. of cobalt gives a smooth coating, but if less cobalt is present the coating is rippled, and if more is added "pimples" are produced. Nickel acts in the same way, but a higher percentage (about 0.1) is required.

Coatings of the tin-silver eutectic (3.5 per cent. of silver) on copper show ripples, and as with pure tin their formation can be prevented by adding about 0.04 per cent. of cobalt. Silver itself will smooth out the tin coating if somewhat more than 3.5 per cent. is present; smooth coatings have been obtained with the 3.7 per cent. alloy.

The copper which dissolves in the tin during dipping also smooths out

* In practice additional control is often exercised by means of rolls, or by holding in hot oil.

the ripples when it is present in the correct proportions. A bath containing 1.1 per cent. of copper produces smooth coatings, and that amount of copper is also effective in the presence of up to 10 per cent. of bismuth, where, in its absence, rippled coatings are obtained.

Recent work²⁶ has shown that tin forms eutectics with Ag_3Sn (3.5 per cent. Ag), with Ni_3Sn_2 (0.18 per cent. Ni) and with Cu_6Sn_5 (less than 1 per cent. Cu). The similarity of nickel and cobalt suggests that cobalt will probably produce similar alloys to nickel. This is supported by the duplex structure of tin containing very small amounts of cobalt, and by the rapidity with which the melting-point of tin rises with additions of cobalt.

It appears, therefore, that those alloys which produce coatings free from ripples possess a freezing range within which crystals of compound are precipitated. It is suggested that these tiny crystals act as a kind of "grit" in the molten metal, preventing that movement which, when unimpeded, results in ripples. Even when the composition of the bath is correct, the dipping must be carried out at the correct temperatures, if smooth coatings are to be produced. When the specimen is tinned at too low a temperature the coating is "pimply," presumably because the

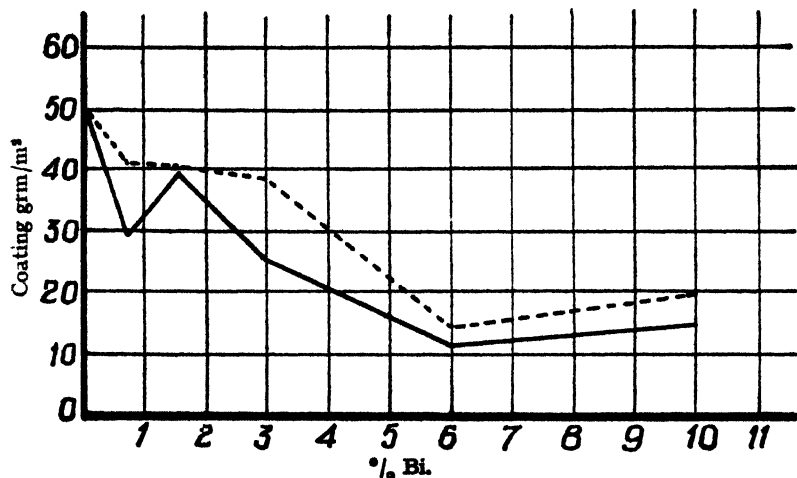


FIG. 4.

compound crystals have agglomerated and produced grit which is too large. Tinning at too high a temperature, on the other hand, produces coatings which are rippled. This is readily understood in view of the fact that a coating of pure tin does not ripple immediately after the specimen is withdrawn from the bath, but remains smooth for a short time. It is clear that the grit must be produced before the rippling movement begins, since it has no power to smooth out ripples once they are formed. In the absence of grit the coating can be kept smooth if it is quenched before rippling has begun. This is true for tin and tin alloy coatings.

For the thin copper sheet used in this investigation, the range of dipping temperature giving a smooth coating with tin containing 1.1 per cent. of copper was found to be 240°-280° C. With increase in copper it appears that the lower temperature must be raised. This point is being investigated.

The reasons for the non-appearance of rippling in many hot-dipped coatings are obscure. Surface tension does not appear to be the decisive factor. The prevention of rippling in tin by the addition of certain

²⁶ D. Hanson, E. J. Sandford and H. Stevens, *J. Inst. Metals*, 1934, **55**, 115.

amounts of copper, cobalt, nickel, etc., has been ascribed to an increase in the viscosity of the tin due to the precipitation of crystals of compound. The absence of ripple in zinc coatings may be due to the higher viscosity of molten zinc²⁷ in comparison with molten tin.^{28, 29, 30}

It seems clear that smoothing out of the tin coating is the result of precipitation of "grit" soon after cooling has begun, and just before rippling would commence in the absence of any "grit." During the time that elapses between the commencement of cooling and the precipitation of "grit," the tin is very fluid and can be partially shaken off the specimen. In fact it appears that the majority of "excess" tin is removed almost at once, and for a given temperature of dipping (*i.e.* initial viscosity) there is a definite "natural" weight of coating, whether grit-forming material be present or not. This is supported by the results shown in Fig. 4.

The full line shows the relation between weight of coating and percentage of bismuth in the tin, copper being absent; the dotted line refers to the same alloys containing a little over 1 per cent. of copper. The coatings free from copper were rippled; those containing copper smooth. The tinning procedure and temperature of dipping were the same for all specimens. The viscosity of the tin-bismuth alloys is probably less than that of pure tin.³¹ The surface tension of tin is lowered progressively by additions of bismuth.³² The rippling of the coatings was more noticeable the higher the bismuth content, indicating that the drop in viscosity more than balances the decrease in surface tension.

Annealing and Quenching.

The copper and bronze plates used in heat-exchangers in the dairy industry are wiped after tinning, a blow-lamp being used to keep the work hot whilst this is being done, so that a coating consisting almost entirely of tin-copper alloys is produced. The more usual heat-treatment for hot-dipped coatings is quenching, which may be carried out before or after the coating has solidified or "set."

The majority of tinned steel articles, except tinplate, are quenched while the coating is still molten. Various quenching media, *e.g.*, water containing soap or oil, kerosene, high flash-point oils, etc., are used. Quenching is an operation demanding considerable skill if bright, smooth coatings are to be produced. The correct rate of quenching keeps the level of the water about 2-3 mm. below the front of the wave of crystallisation of the tin. Too rapid quenching gives a frosty surface. A method which has given excellent results in the laboratory is an "air" quench. Jets of air are applied to both sides of the sheet a few millimetres above the tin surface as the object is slowly lifted out. By this means a smooth, thick coating can be produced without the usual drainage bead at the bottom.

According to Imhoff³³terne coatings must be quenched if a spongy coating is to be avoided. He states that the operation is a delicate one and that the alloy should just be set at the instant the pieces are quenched, or perhaps an instant before they go into the water.

Spangle.

The name "spangle" is given to the flower-like markings which appear on galvanised sheet. Similar markings can occur on coatings of other metals and may occasionally receive other names.

²⁷ L. Losana, *Notiz. Chimico-Industriale*, 1927, 2, 63-66.

²⁸ A. Benias and F. Sauerwald, *Z. anorg. Chem.*, 1926, 161, 51.

²⁹ V. H. Stott, *Proc. Physic. Soc.*, 1933, 48, 430.

³⁰ R. Arpi, *Int. Z. Metallog.*, 1914, 8, 142-168.

³¹ F. Sauerwald and K. Töpler, *Z. anorg. Chem.*, 1926, 157, 117.

³² F. Sauerwald and G. Drath, *Z. anorg. Chem.*, 1927, 162, 301.

³³ W. G. Imhoff, *Iron Trade Rev.*, 1928, 83, 1558.

The material known as "terne" plate is steel coated with lead containing 12 to 50 per cent. of tin. During the solidification of the coating a characteristic surface network or crystal pattern is formed which is analogous to the spangle on zinc-coated sheet. This appearance is known as "mottle" (not to be confused with the mottle in tinplate) and, according to Rawdon (*loc. cit.*, p. 174) the size of the network increases with the thickness of the coating, so that it serves a rather useful purpose therefore, as an index of the weight of the coating. According to Mantell,¹¹ the fineness or coarseness of the mottle can be controlled by the rate of cooling and is also affected by the presence of antimony in the terne alloy.

Coatings of pure tin on steel also show a large spangle when the coating is thick, the markings being similar to those produced by zinc containing lead. Fig. 5 * shows crystal boundaries on unetched tinplate. The spangle due to change of volume on solidification must not be confused with the marked crystal pattern sometimes found on tinplate which is caused by etching in acid fumes from the flux.

Since, as opposed to zinc coatings, tin coatings are desired as unmarked as possible, little work has been done on the formation of large spangles in tin. It has been found, however, that the addition of bismuth causes the appearance of large spangles. These are similar to those found in zinc containing lead, except that the edges of the grains are marked by ridges instead of depressions. This is undoubtedly due to the expansion on solidification of the tin-bismuth eutectic.

Mohr and Schulz¹² have described the etched structure of tin coatings produced under different conditions of cooling. One of the most interesting structures, which has also been observed by the writer, is termed by them "arched" crystals. It consists of concentric rings of tiny crystals, the rings being alternately light and dark as if solidification had taken place in waves. This structure occurs also inside the natural polygonal spangles on the coatings containing bismuth, the rings terminating abruptly where they meet the spangle boundaries. When coatings which have been air quenched are etched, the bands of crystallites are almost perfectly straight and are at right angles to the direction in which the sheet was lifted out of the tin.

Summary.

Existing theories of the factors involved in the formation of hot-dipped coatings are reviewed and attention is directed to the attraction between the liquid and solid metals as a prime cause of wetting. In general, affinity between base and coating metal results in the formation of an inter-metallic compound or solid solution. Additions to the molten metal sometimes lead to considerable alterations in the structure of the coating. The effects of certain additions to tin on the alloy layer are described. The relation of the fluxing operation to the production of the coating is discussed. Some experiments with unusual fluxes (phosphorus and hydrogen) are reported. Attention is directed to the phenomena of rippling and spangling occurring during the solidification of the coating.

The author wishes to thank the International Tin Research and Development Council for permission to publish this paper, and their Director, Mr. D. J. Macnaughtan, for many valuable and stimulating discussions and the interest he has taken in the work described. Thanks are also due to Mr. W. E. Hoare, B.Sc., for Figs. 2, 3 and 5.

¹¹ C. L. Mantell, *Tin*, p. 249.

¹² W. Mohr and M. Schulz, *Milchwirtschaftlichen Ztg. Stendal*, 1930, 1037-1124.

* Plate LXXVII.

GENERAL DISCUSSION.

Dr. L. Tronstad (*Trondheim*) said: The method of Professor Glazunov might be very useful for studying certain types of metallic coatings, also from a practical point of view. However, the method is based on the assumption of a homogeneous anodic current density, which may not always hold good. Further the method seems unable to tell anything about the distribution of the thickness or the homogeneity (porosity) of the coating, which factors are of the greatest importance for the practical service of coatings.

Mr. A. W. Hothersall (*London*) said: The method for determination of thickness of coating described by Professor Glazunov would appear to be applicable to wires, where an approximately uniform current density can be secured, but it is not clear that it would give reliable results for flat or irregularly shaped specimens. It would appear that the less uniform the distribution of current density, the more gradually would the potential rise since certain areas of the specimen would be stripped of deposit before others. Similarly it would appear that the results would be difficult to interpret if the coating were not uniform in thickness. The probable effects of lack of uniformity of current distribution, or of thickness of deposit on the potential difference time curve would appear to render difficult any conclusions as to the presence or thickness of compound layers, except possibly with hot-dipped coatings on wires. With certain well-known exceptions (for example, copper coatings on zinc, or zinc on copper, where interdiffusion occurs at room temperature), neither microscopic nor X-ray examination have revealed the presence of any compound or alloy layer between an electrodeposited coating and the basis metal. That such a layer exists over a thickness of a few atoms is possible, but it is unlikely that an electrochemical method such as that suggested by Professor Glazunov would be capable of detecting it.

Professor Glazunov, in reply, said: The method can be used only for those coatings in which the coating protective metal sacrifices itself, *i.e.*, for coatings having a higher potential than the base metal; for this group of coatings the porosity and discontinuity are of no importance.

For coatings of the second type having a smaller potential than the base metal, for which the porosity and continuity is of the highest importance, the method (a variation of the method proposed) is submitted¹ which shows not the total thickness but the pinholes and thin places of the coating. The method proposed was proved not only for electroplated or galvanized wires but also for sheets²; comparative tests with other methods have shown that the results are very satisfactory.

Mr. A. W. Hothersall (*London*) said: Dr. Reininger states that "metallic coatings produced either by galvanisation or by spraying are never firmly bonded to the base metal on which they have been deposited." My limited experience of sprayed coatings confirms this statement, but it is not true for coatings produced by electrodeposition.

¹ A. Glazunov, *Une nouvelle méthode pour déterminer la qualité de la couche métallique sur les objets métallisés*. *Chimie et Industrie*, XIV^e Congrès, Paris, 1934.

² J. Teindl, *Testing of galvanized iron sheets by the method of Professor Glazunov*, *Mining Journal*, *Hornický Věstník*, Prague, 1935.

Two of the papers to this Discussion show examples of continuation of micro-structure of the basis metal by an electrodeposit. Such deposits are strongly adherent to the basis metal and their detachment requires a stress sufficient to rupture the base or the deposit, whichever is the weaker. With the exception of one or two metals, for which satisfactory methods of treatment have not yet been found, similar results can be obtained where the microstructure is not seen to be continued across the interface. Thus, quantitative adhesion tests of nickel deposits formed on steel of various types have shown that loads normal to the interface of 20-30 tons per sq. in. are required to detach the deposit.³ Whilst this is not an important part of Dr. Reininger's paper, it is felt desirable to correct any misunderstanding that might arise as a result of his introductory paragraph.

Mr. W. E. Hoare (*London*) said: The "mottled" layer in tin-coatings on steel mentioned on page 1280 of the paper cannot be considered to be an intrinsic property of the FeSn_2 layer. Mottle does not occur when sheets are tinned through palm-oil, as in the processes used in producing heavy tin coatings. It appears that the presence of such patterns depends upon the use of a chemically reactive and ebullient flux. These conditions are established in normal sheet tinning machines, the film of water carried into the flux-bath causing ebullition by the evolution of hydrogen chloride. It is possible that the full mottle effect is already on the sheet before it reaches the flux-tin interface, the selective compound-forming reactions then rendering the pattern visible to the eye. The author has mentioned that a similar effect is sometimes obtained in coatings on copper. A knowledge of the conditions under which such effects were obtained would be exceedingly valuable.

The specimen illustrated in the photomicrograph (Fig. 1) * yields some interesting facts connected with the possible formation of duplex compound fringes.⁴ It is reasonably certain, as the author says, that such duplexity will not occur in normal tin coatings on steel. The rate of reaction between tin and copper however, is considerably more rapid. The specimen illustrated is a tin coating on copper that has been annealed at 375° C. for 5 hours. The photomicrograph shows five phases: from the top downwards:—

Eutectic (Black), " CuSn ," ϵ (White), Cu_3Sn , η (Grey), Cu_4Sn , δ (White), and copper.

From consideration of this specimen it would appear to be possible in favourable circumstances to pass across a binary equilibrium diagram along an isothermal, obtaining in this particular case, the five phases already mentioned, plus α solid solution, *i.e.*, a diffusion zone.

H. Reininger (*Leipzig*), in reply, said: I would like to make the following reply to the remarks of A. W. Hotherhall. My hints as to the unsatisfactory behaviour of galvanic deposits were not intended to deny any possibility of preparing really stable coatings at all. The papers by A. W. Hotherhall, A. M. Portevin and M. Cymboliste show us how coatings possessing an extremely tight connection with the base can be produced. But these were coatings grown in the laboratory with very elaborate precautions. My remarks were concerned with technical products; and my experience is that technical coatings never stand a long use. At least, I never came across a nickel or chromium coating—for instance on motor-cars or bicycles—which would not be affected by variable weather-conditions and similar

³ *Trans. Electrochem. Soc.*, 1933, 64, 69.

⁴ See also Jones and Hoare, *J.I.S.I.*, 1934.

* Plate LXXVII.

influences. Sooner or later—after some years, but frequently only after some months—the coating begins to split off and the base is opened to corrosion. My criticism was based on these practical observations.

Mr. Daniels, in reply, said: Mr. Hoare's suggestion that the steel-tin reaction develops the mottle effect produced by reaction of the sheet with a flux which is full of gas pockets is very interesting. Tinned copper does not show such a well-defined mottle effect as tinplate, but indications of the pattern have been noticed on specimens tinned with an ebullient flux.

It is, of course, well known that under favourable conditions it is possible to obtain a number of the binary phases in a coating, and Mr. Hoare's photomicrograph gives an excellent illustration of this. I consider, however, that the time and temperature of the treatment required to produce this are so far removed from those of tinning practice (where temperatures are usually under 300° C. and times are of the order of seconds) that it would be unsafe to make any inference with respect to the structure of hot-tinned copper. A series of experiments on the effect of time and temperature on the rate of solution of copper in tin and on the nature of the alloy layer formed for short times of immersion at moderate temperatures is in progress and it is hoped to be able to report on these at a later date.

Professor Finch, in summarising the discussion: Much of our time has been devoted to the discussion of the electron diffraction method for the study of thin metal films and surfaces. As an instrument, the electron diffraction camera is still in the initial stages of development, and its potentialities are only gradually being revealed; but its contributions to our knowledge of surface structure are already such as to command respect. It has settled the Beilby layer controversy, disclosed the existence of hitherto unsuspected substrate effects and afforded some insight into the mode of absorption of gases by metals. Future progress is largely dependent on our ability to interpret the electron diffraction pattern; and in connection with this the importance of further systematic study of single crystal diffraction effects cannot be too strongly emphasised.

Although appearing as an ardent protagonist of this new and powerful weapon of investigation, I would not wish to leave you under the impression that in my view electron diffraction is going to supersede the methods hitherto employed. Far from it; indeed, the beautiful examples of the power of optical methods, and above all of the microscope, which have been brought before us at this meeting speak convincingly in favour of the closest co-operation between electron diffraction and the optical methods.

CONCLUDING REMARKS.

BY DR. C. H. DESCH.

The discussion on the study of surfaces by means of diffracted electron beams has been very fruitful, and has been summed up by Professor Finch, whose contribution will serve as a monograph for those who are interested. It has been made clear that although there is still room for differences in regard to the interpretation of some of the experimental results, this new method of investigation is remarkably helpful, and is probably the most powerful means as yet available for the examination of surface films.

On the vexed question of the Beilby layer on polished surfaces, the

are all factors influencing the hardness, and their relations to one another demand further study.

That colloidal matter affects the texture and hardness of electrolytic deposits, partly by checking the growth of crystals on the cathode, and partly through its dispersion throughout the deposit, is generally agreed. The nature of the particles which may be included, and their effects in causing abnormal growths, have been examined systematically by Professor Kohlschutter, whose account of "somatoids" will be found valuable in discussing the influence of factors which influence growth. The mechanical effects of such included matter were shown by Professor Portevin and M. Cymbolste, whilst Professor Glazunow, in the course of the discussion, called attention to previous publications in which he has indicated a mechanism for the influence of dendritic growth on the structure of deposits. New facts were brought forward concerning the conditions under which the crystal structure of the basis metal may be continued by the deposit, and Professor Portevin rightly called attention to the resemblance between this effect and the well-defined parallel associations in minerals. Reference may here be made to the important papers of Barker⁵ on parallel growths of one kind of crystal on another, and to later work on the same subject⁶. Such work has made it clear, in a large number of instances, how far the two lattices may differ and yet allow parallel growth to take place.

The papers by Professor Schlotter and Dr. Glasstone showed that it is not necessary that actually precipitated matter should be carried into the cathode for interference with crystal growth to take place, since positive complex ions may pass to the cathode, and there decomposing produce insoluble substances which produce the effect. In this connection reference was made to a paper⁷ which described experiments on the deposition of silver on a spherical cathode consisting of a single crystal of the metal. By this means the growth of the various faces could be studied individually, and the effect of foreign ions observed. The results indicated that preferential adsorption on certain faces occurred, causing a change in habit, since growth perpendicularly to a face covered with an adsorbed layer is slowed down. On such lines, working with single crystals, it may be possible to obtain a more direct insight into the mode of building up of electrolytic deposits of metals.

The papers collected together, and the full discussion which followed on the reading of them, provide a very complete survey of the subject chosen, and the opportunity of comparing the views of different investigators has been most valuable. As regards methods of investigation, it is clear that whilst the method of electron beam diffraction is invaluable in the examination of very thin surface layers, X-rays, methods depending on the optical properties of surfaces, electrolytic potential measurements, microscopical examination, and the determination of mechanical properties such as hardness, are all essential in the study of the very numerous factors which determine the structure of surfaces and metallic coatings. It may be suggested that a study of the chemical properties of individual metallic crystals and of the adsorption of foreign ions, atoms or molecules by their several faces may be found to throw much light on the problem, since the building up of a coating resolves itself at last into a process of the growth of metallic crystals.

⁵ T. V. Barker, *Trans. Chem. Soc.*, 1906, 1120.

⁶ C. W. Bunn, *Proc. Roy. Soc.*, 1933, **141A**, 507.

⁷ Erdey-Gruz, *Z. physikal. Chem.*, 1935, **172A**, 157.

PLATE I

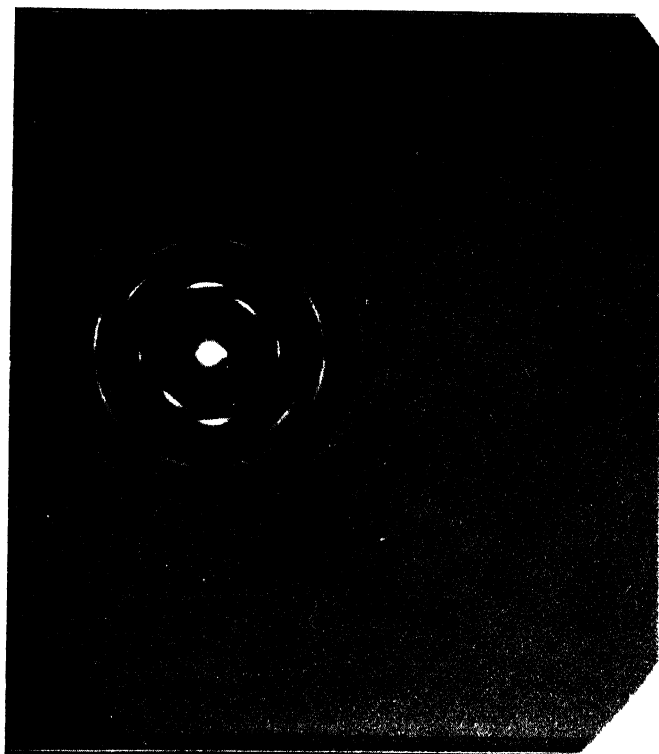


FIG. 1 — Diffraction Pattern of gold foil at 8.5 kilovolts
(See page 110.50)



FIG. 2 — Copper- oriented layer
(See page 110.3)

PLATE II.

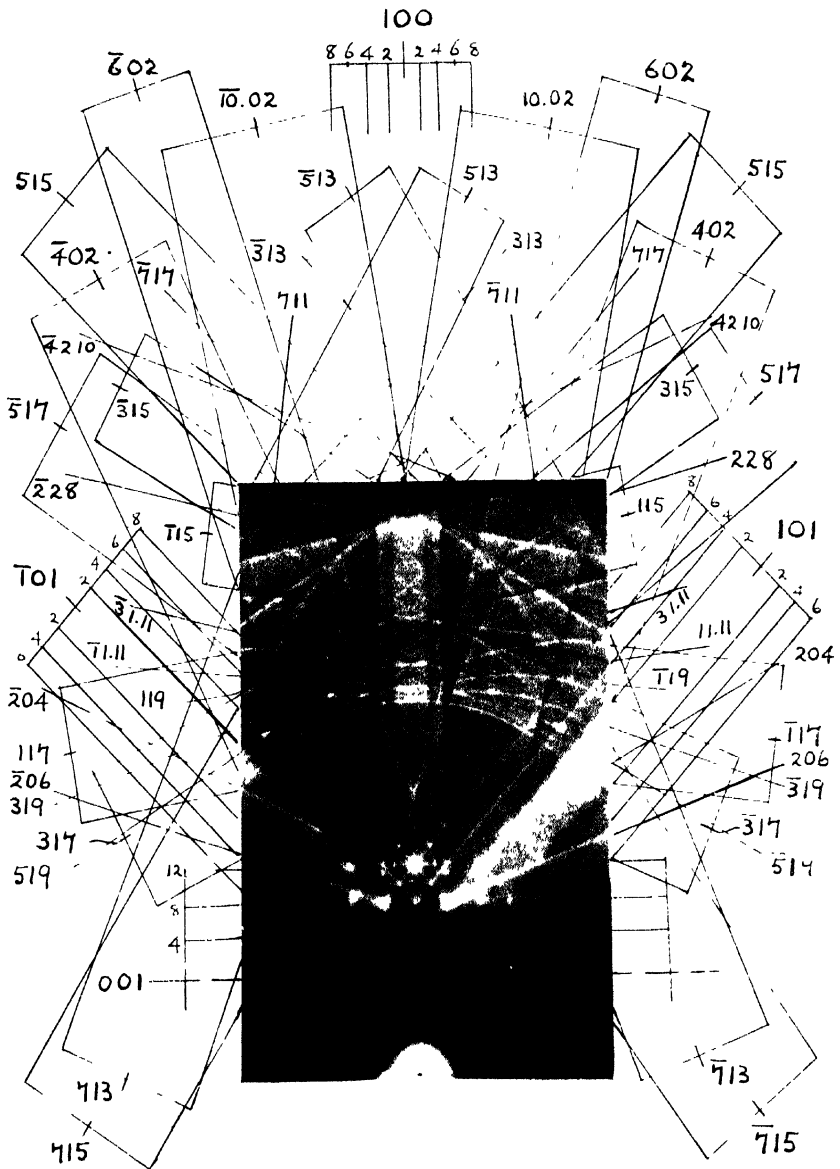


FIG. 7.— CaF_2 cube face; $\phi = 0$.

{For Plate II to XXVIII see pages 1051 to 1080}

THE END III

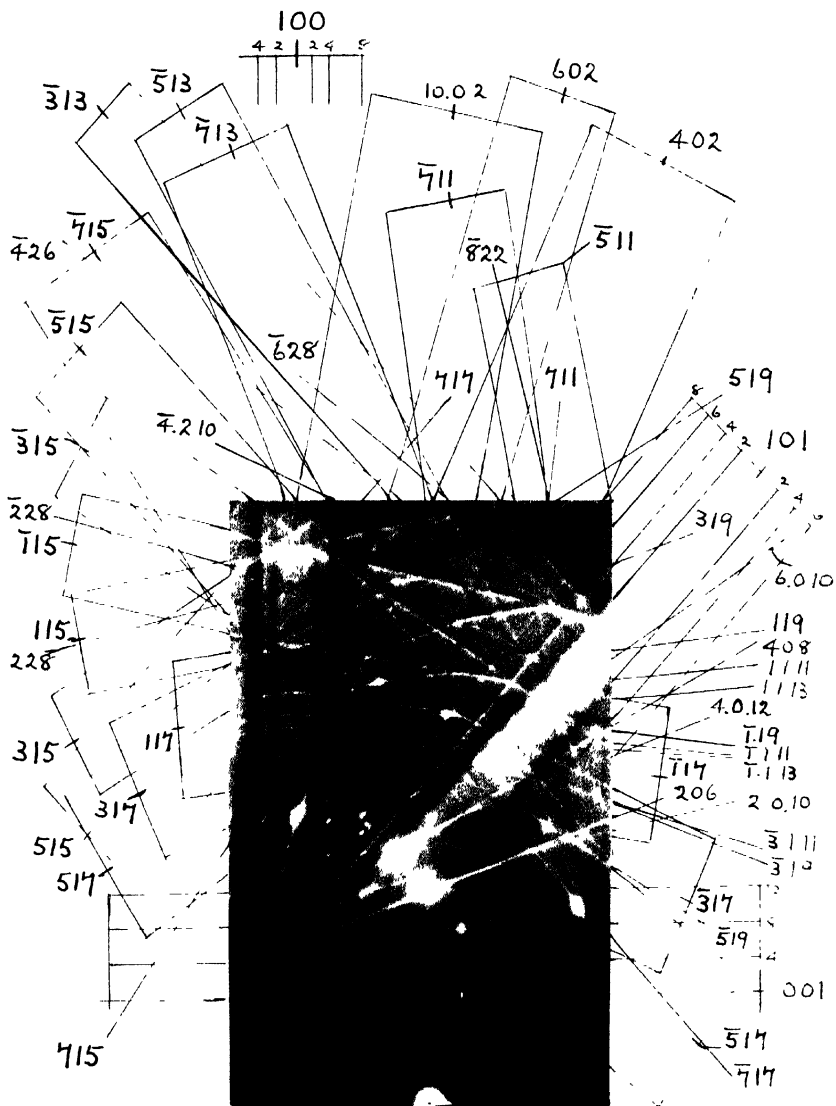
FIG. 11. CaF_2 cube face, $\phi \cong 1$.

PLATE IV.

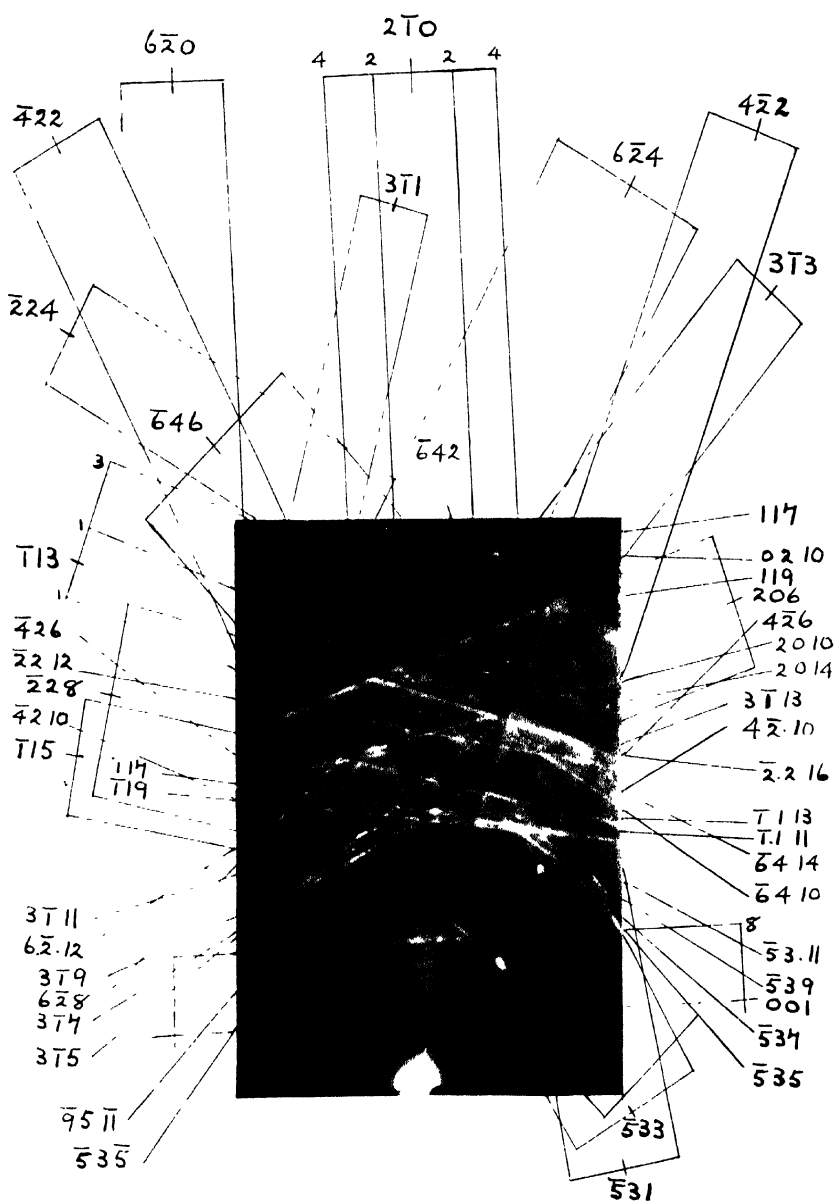
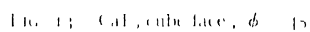


FIG. 12. CaF_2 cube face. $\phi = 20-34^\circ$



107

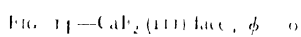
FIG. 11— CaH_2 (111) face, $\phi = 0$

PLATE VII

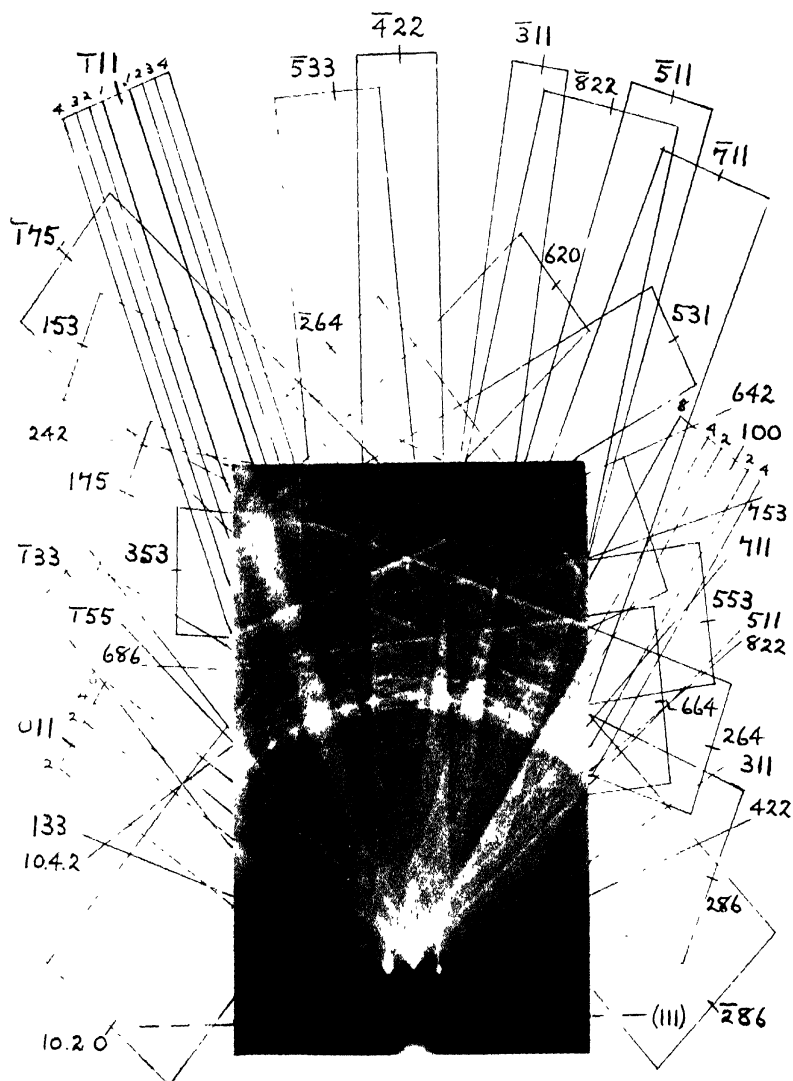


FIG. 15. CaF_2 (111) face, $\phi = 30^\circ$

PLATE VIII

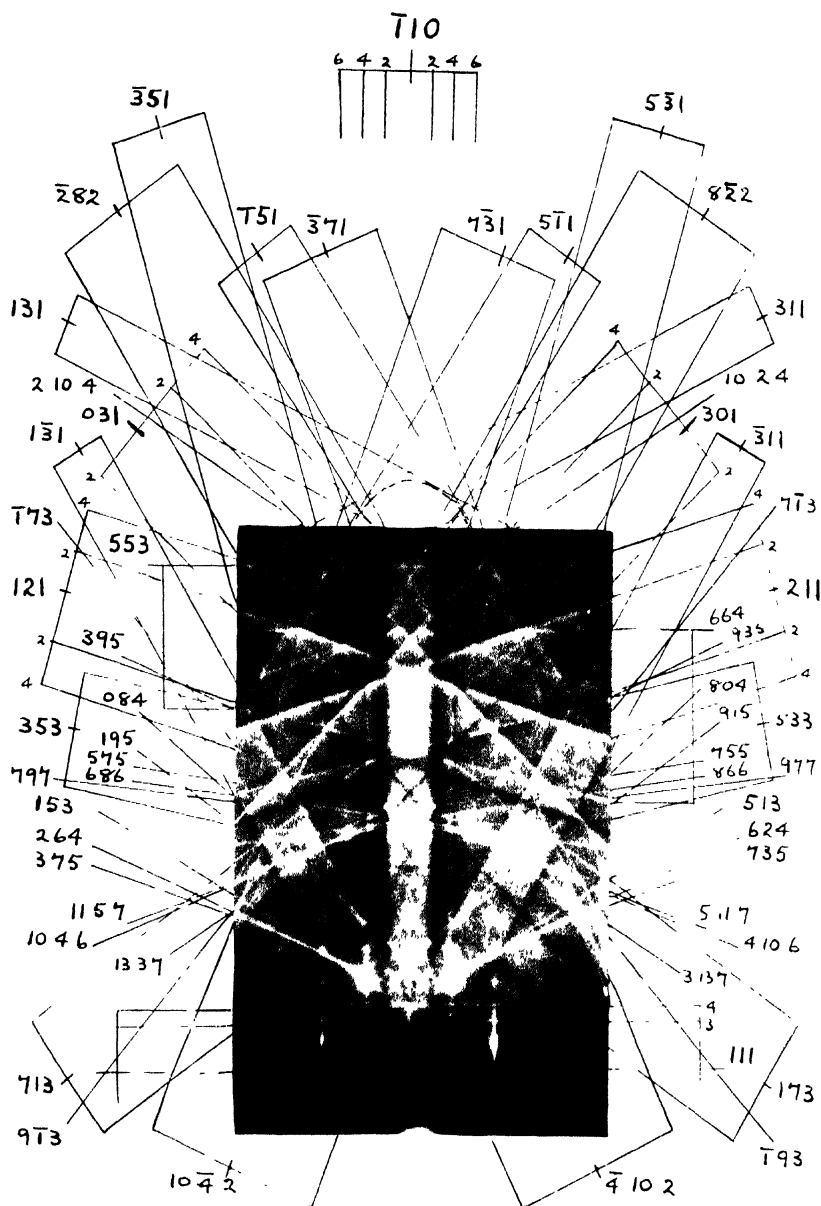


FIG. 16. CaF_2 (111) face, $\phi = 0^\circ$.

PLATE IX



Fig. 17 - Cobalt foil δ_0 - Pattern distorted by $\frac{1}{2}\pi$ shear in $\frac{1}{2}$ between specimen and plate.

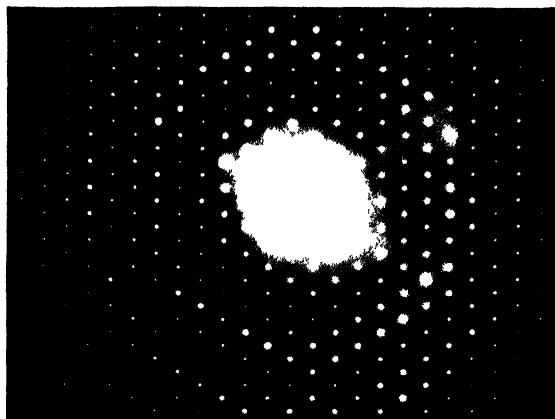


Fig. 18 - Mica single crystal viewed along c axis. Note faint Laue rings and wide zero order maximum.

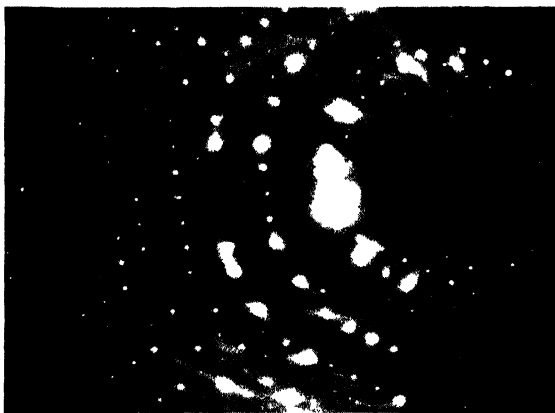


Fig. 19 - With a thicker mica film secondary scattering effects occur and Laue rings become sharper.

PLATE X

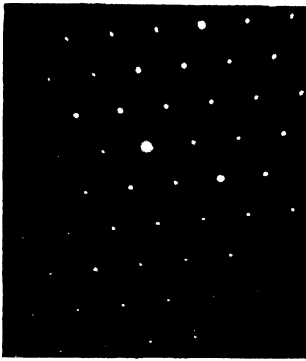


FIG. 22 Pure cross-grating pattern from mica



FIG. 23 Distortion in pattern produced by inclining mica film



FIG. 24 Area of exposure film without perfect clarity showing the comparatively better effect of a condenser is still to be seen

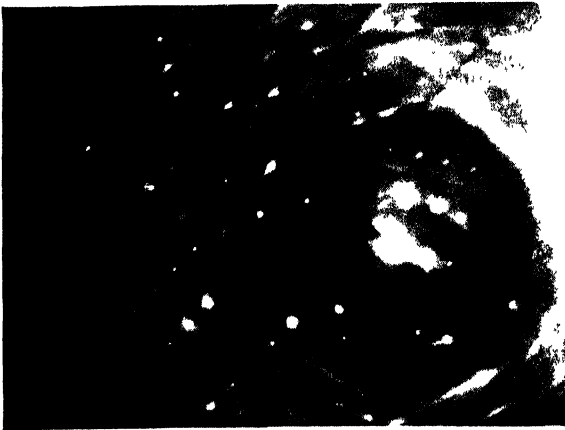


FIG. 25 A still thicker mica film produces intense secondary scattering effects, but many primary spots are still visible

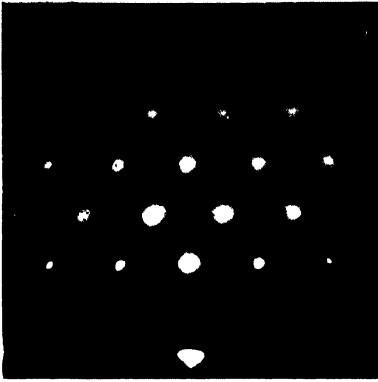


FIG. 24. "Cross-grating 'reflection'" pattern from a (110) face of ZnS etched with dilute HNO_3 , $d = 0$.

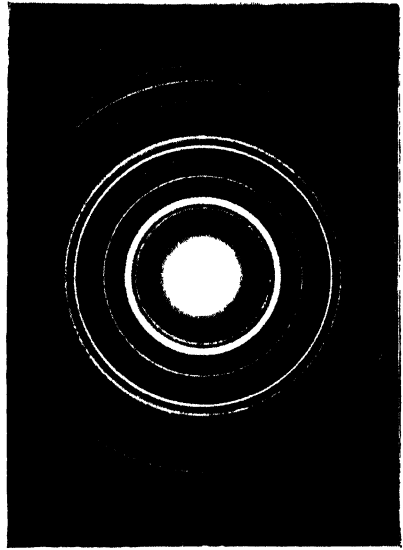


FIG. 25. ZnO, showing normal intensity distribution.

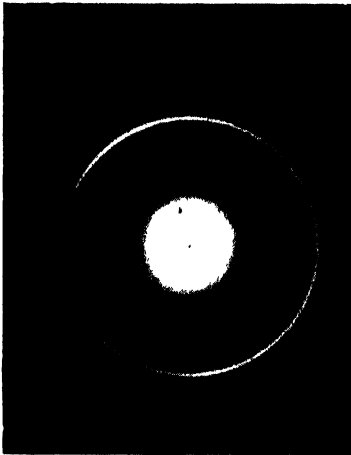


FIG. 26. Colloidal Ag—strong (111) orientation. Specimen plane normal to beam; haloes due to collodion.

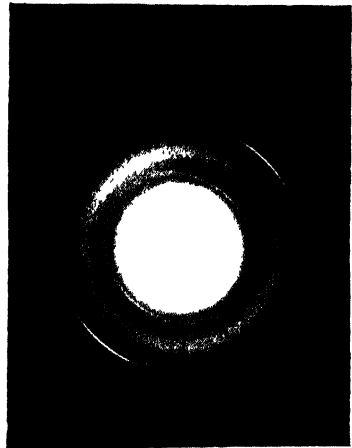


FIG. 27. Same as in Fig. 26, but specimen tilted by about 45° to beam; haloes due to collodion.

PLATE XII.

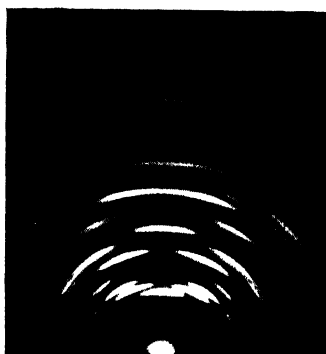


Fig. 28 NiSe_2 , (100) orientation, small crystals

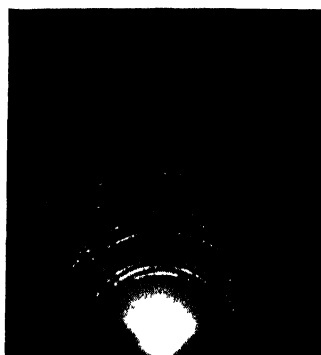


Fig. 29 NiSe_2 , (100) orientation, large crystals

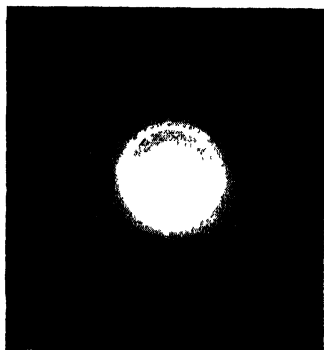


Fig. 30 Collodion, random crystals



Fig. 31 Collodion, approaching single crystal state



Fig. 32 Anthracene, single crystal

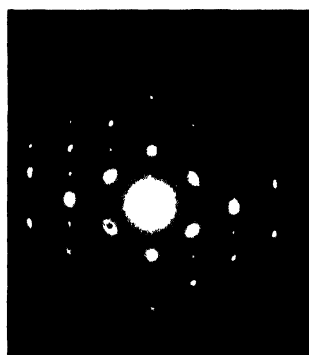


Fig. 33 Stearic acid

PLATE XIII

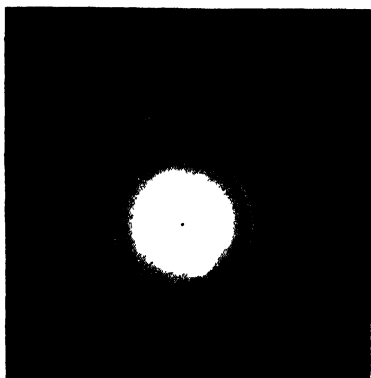


FIG. 34 La the very short arcs are due to celluloid

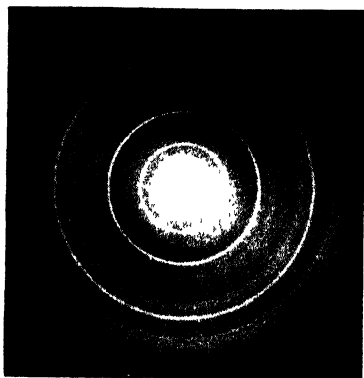


FIG. 35 Mica powder, note black ring

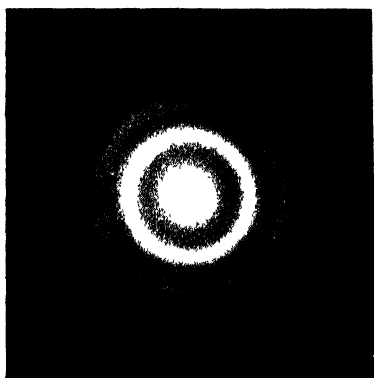


FIG. 36 Sb displaced by Au amorphous

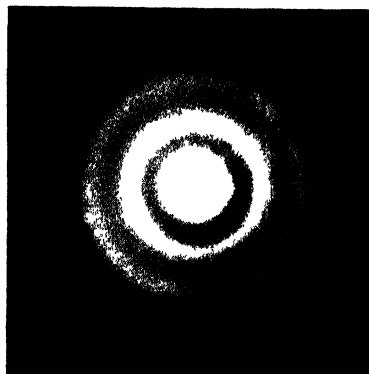


FIG. 37 As cl. dep. on Au, amorphous

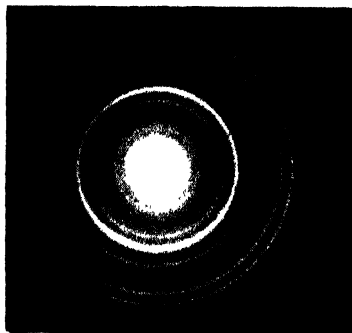


FIG. 38 Fe_2O_3 from an iron atom

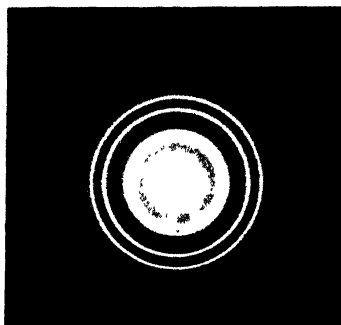


FIG. 39 ThO_2 by decomposition of the nitrate

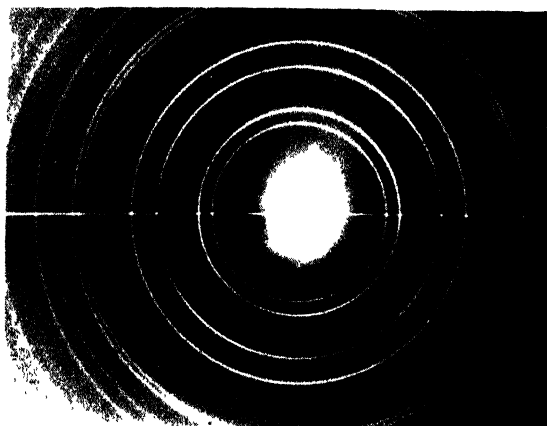


Fig. 46 ---Au foil London.

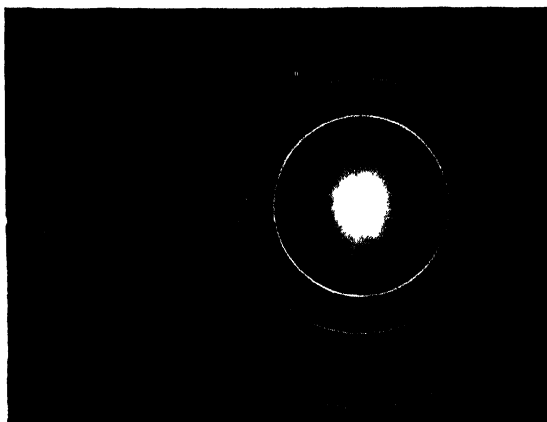


Fig. 47 ---Hitting the foil Fig. 46 in
of particles extra rings and fog
of radiation

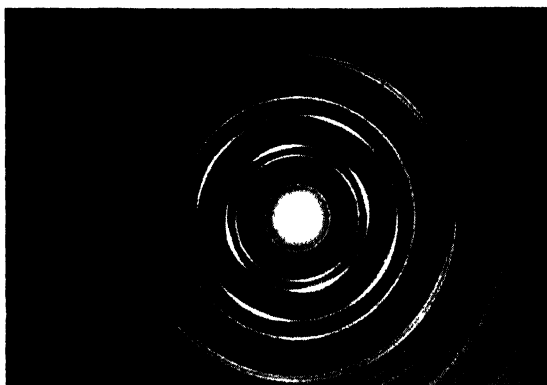


Fig. 42 ---Au foil giving arced pattern
due to being in air continuous
extra rings are obtained

PLATE XV

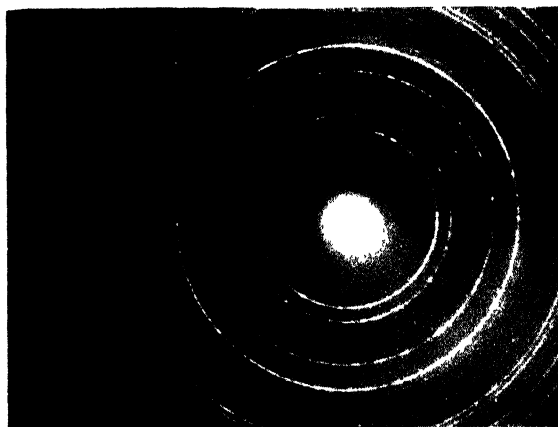


Fig. 43. Arc α_1 phase of a single crystal of iron, orientated by further heating. Note bands and central rings.

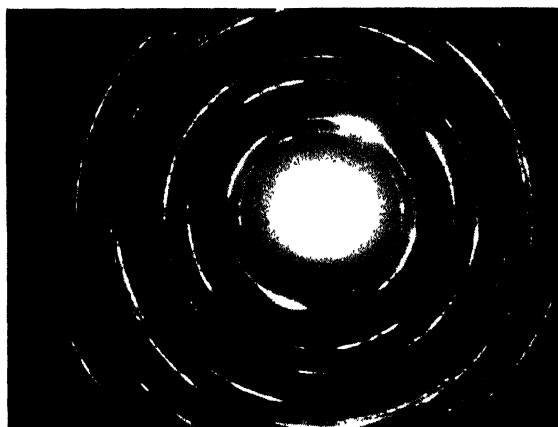


Fig. 44. Crystal growth and orientation produced by heating.

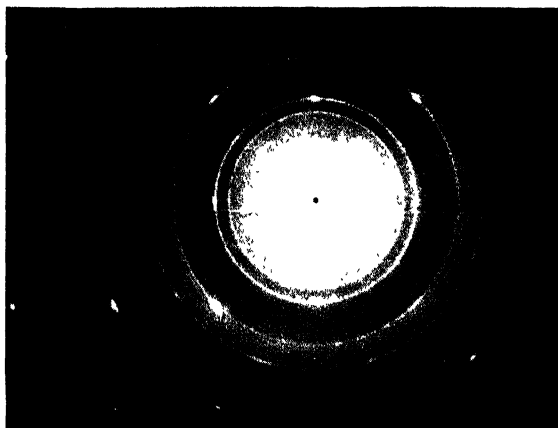


Fig. 45. One single crystal of tool orientated iron, orientated by further heating. Note bands and central rings.

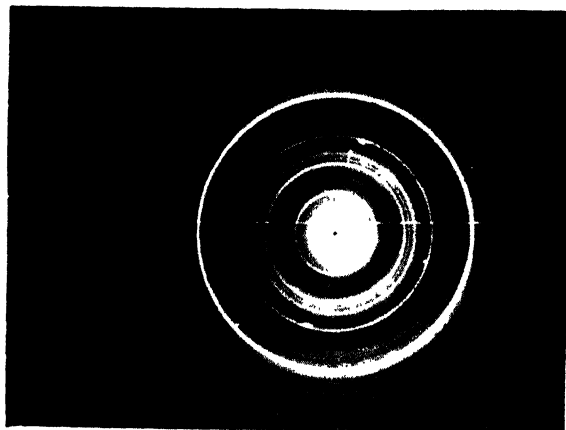


Fig. 48 - With more drastic heating Al_2O_3 is formed though part of the Al crystal still remains

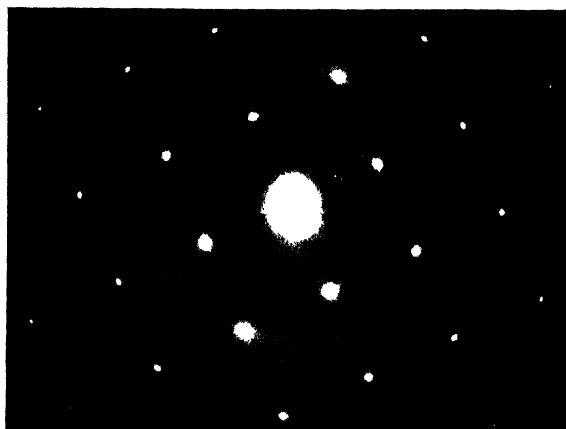


Fig. 47 - After further heating, one large Al single crystal with 100 orientation has been formed



Fig. 49 - The 100 crystal has grown and second has appeared in approximately the orientation

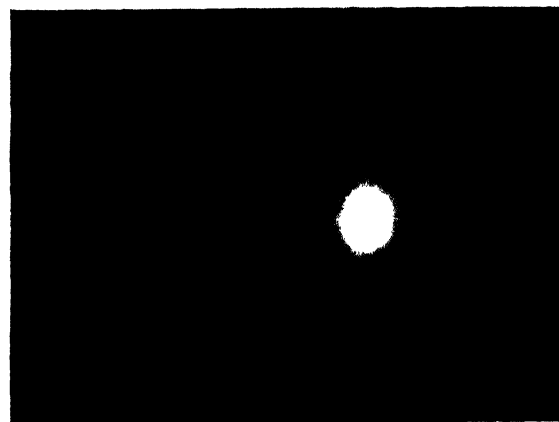


Fig. 4^a NiO formed by oxidizing iron
at 600°C. 100 \times

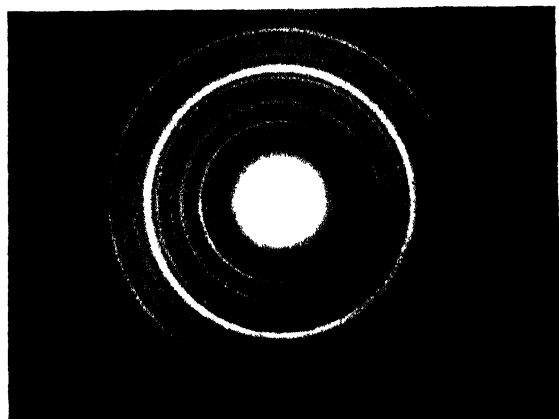


Fig. 5^a Ferrite formed by oxidizing a
cold-chamber cast alloy



Fig. 5^b Ferrite oxide formed during
annealing of steel



FIG. 52. Colloidal graphite, specimen normal to beam

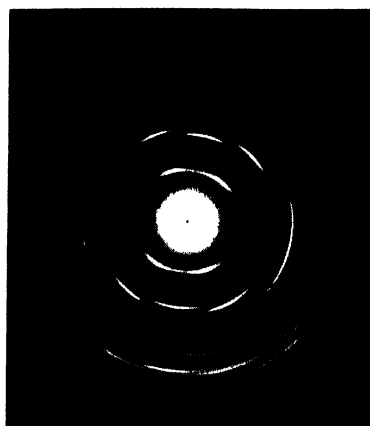


FIG. 53. Colloidal graphite, specimen inclined to beam

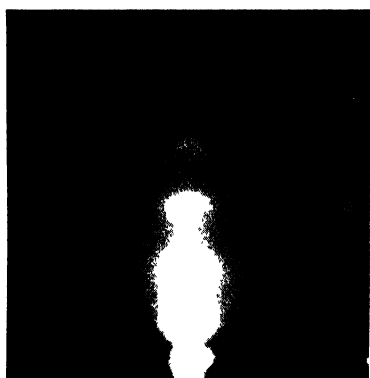


FIG. 54. Colloidal graphite by reflection



FIG. 55. Ordinary graphite.

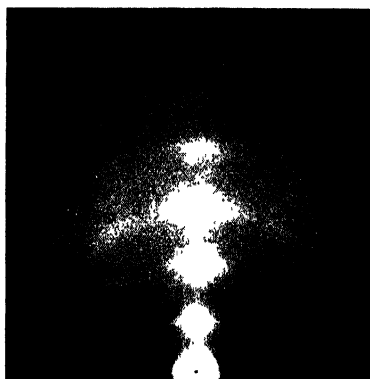


FIG. 56. Graphite on abraded cast iron.

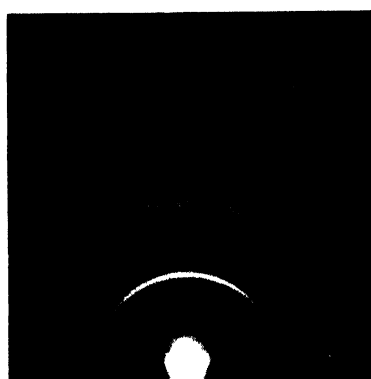


FIG. 57. z-Fe on abraded mild steel.

PLATE XIX

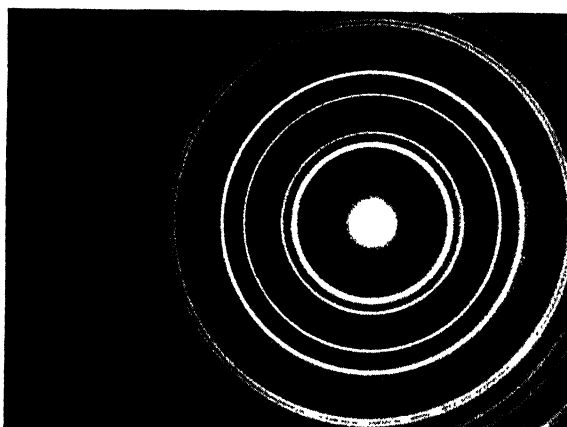


Fig. 58 Ag cl. dep. on Cd, normal orientation, 110° orientation

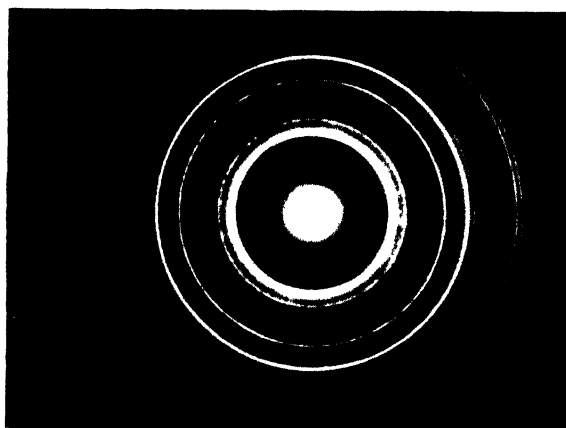


Fig. 59 Ag cl. dep. on Cd, band from 200 to inside 111 ring, 110° orientation



Fig. 60 Ag cl. dep. on Cd, strong bands between 222 and 220, and from 200 to inside 111 rings, also "extra" rings, 110° orientation

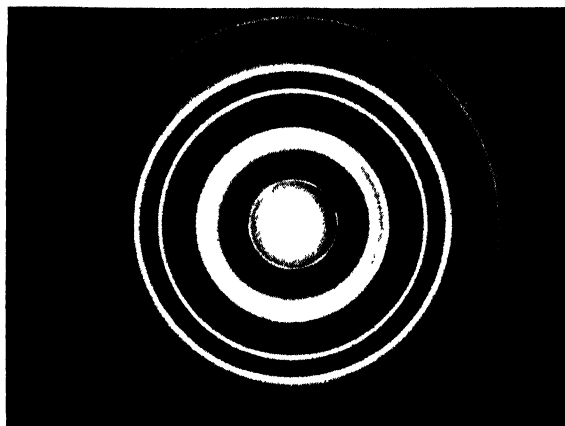


Fig. 63 — Pt el dep on Ni, as in Fig 62, but note hexagonal arcing of "extra" rings

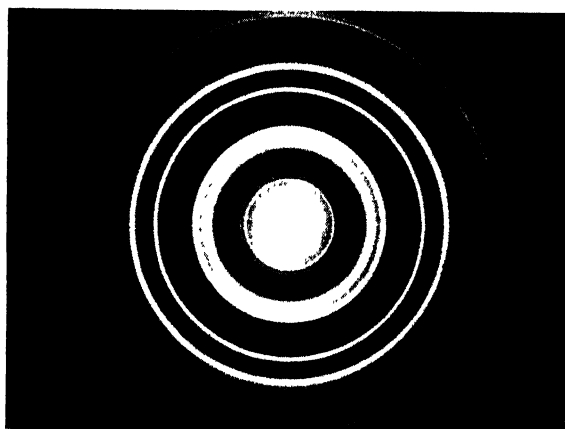


Fig. 62 — Pt el dep on Ni, approximate (110) orientation, two strong "extra" rings and band from 200 to inside 111 ring

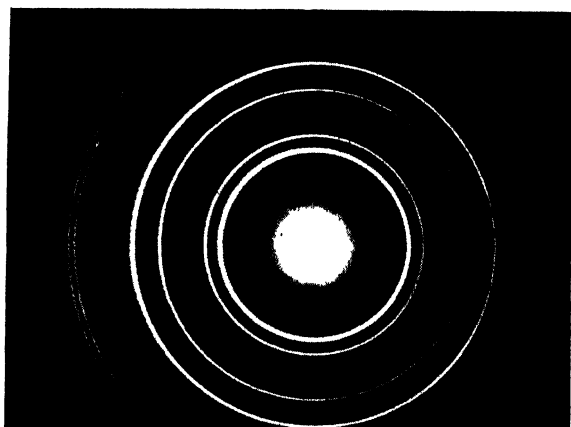


Fig. 61 — Pt el dep on Ni, normal pattern approximate (110) orientation

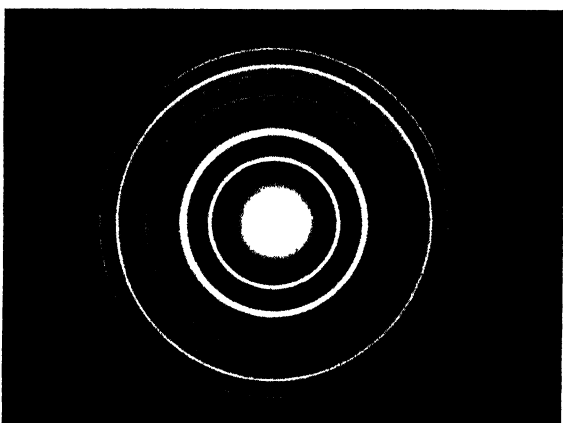


Fig. 64 -- Sn on Cu, normal pattern, $\{001\}$ orientation

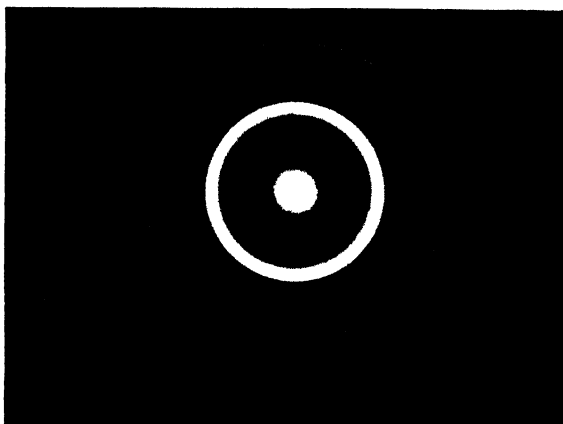


Fig. 65 -- Sn on Cu, note remarkable bands especially inside 2nd strong ring, $\{001\}$ orientation

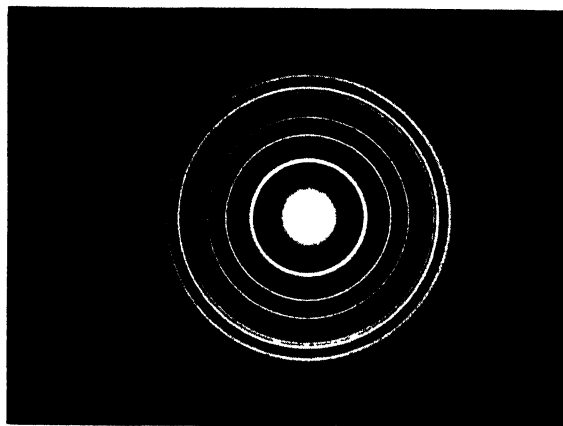


Fig. 66 -- Bi on Cu, normal pattern, $\{100\}$ orientation

PLATE XXII.

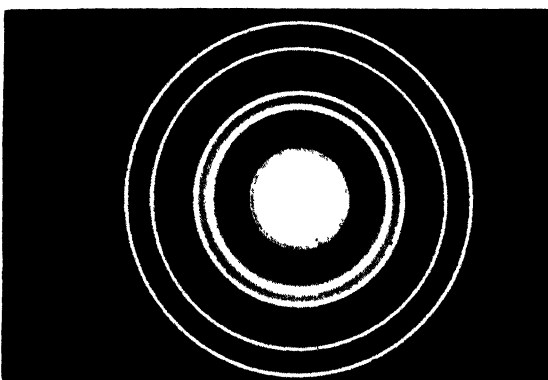


Fig. 67--Ni el dep on Cu, faint band from 200 to inside 111 ring, 2 faint and 2 strong and sharp "extra" rings, $\{110\}$ orientation

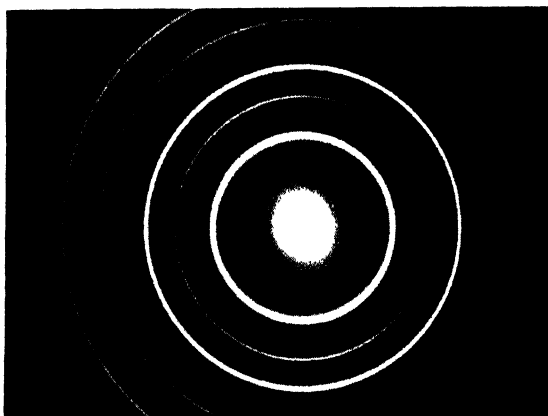


Fig. 68--Fe el dep on Cu, five faint diffuse "extra" ring inside 110 ring, $\{111\}$ orientation



Fig. 69--Co el dep on Cu, two strong bands, one from 200 to inside 111 ring, one between "extra" rings inside 111 ring $\{110\}$ orientation

PLATE XXIII.



FIG. 70 - Sputtered Pt, small crystals, (100) orientation

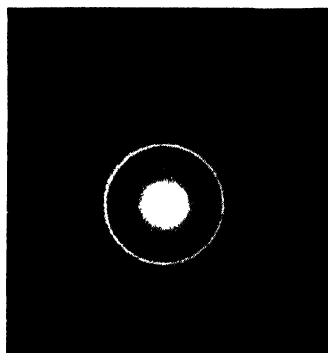


FIG. 71 - Ag chem. dep., note band and "extra" ring



FIG. 72 - Pt "extra" rings by electrodeposition

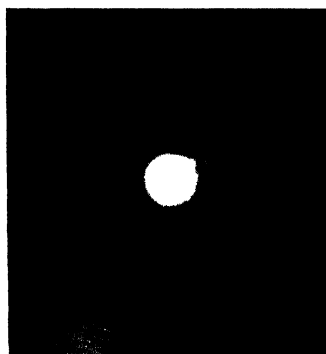


FIG. 73 - Au "extra" rings by heating foil in O_2



FIG. 74 - A copper oxide.



FIG. 75 - Cu_2Cl_2 .

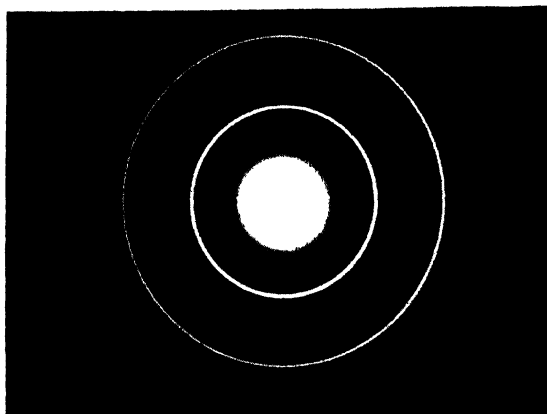


Fig. 78.—Cr el dep on Fe; normal pattern, (111) orientation

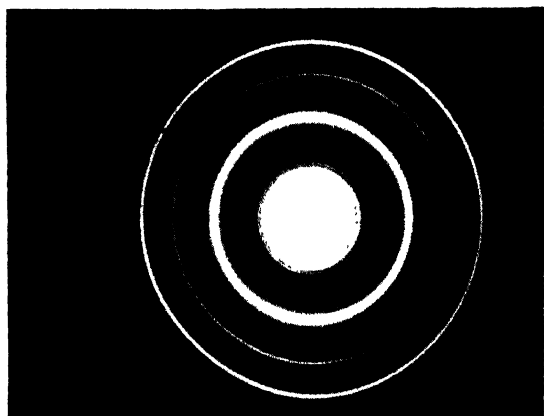


Fig. 77.—Cr el dep on Ni, (111) orientation, two strong "extra" rings, faint band inside 110 ring

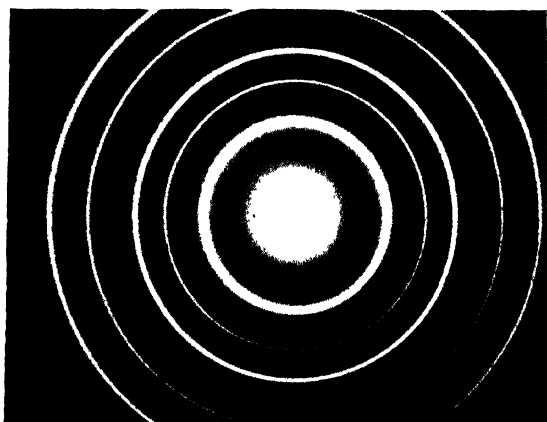


Fig. 79.—Cr el dep on Cu, (111) orientation, faint diffuse "extra" ring inside 110 ring

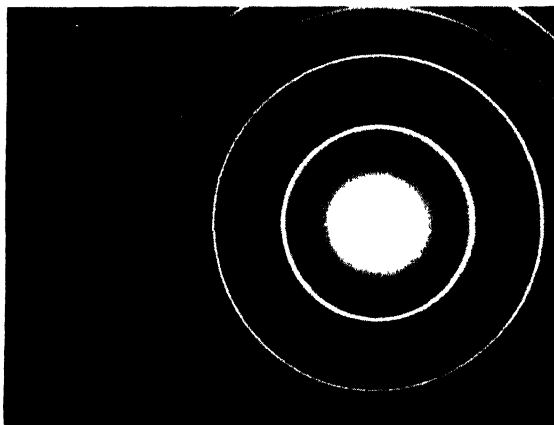


Fig. 79—Cr el. dep. on Si, normal pattern, (111) orientation

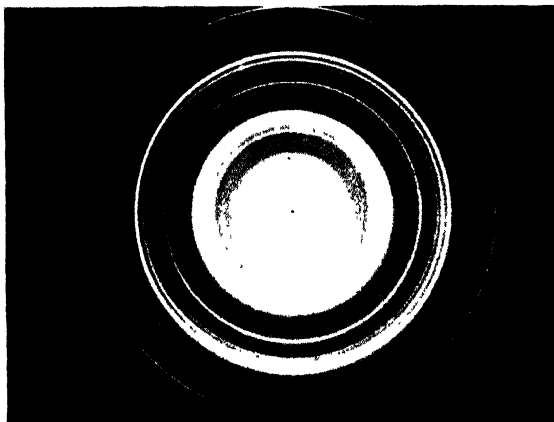


Fig. 80—Cr el. dep. on Sn; "extra" rings and bands, also rings probably due to basis metal

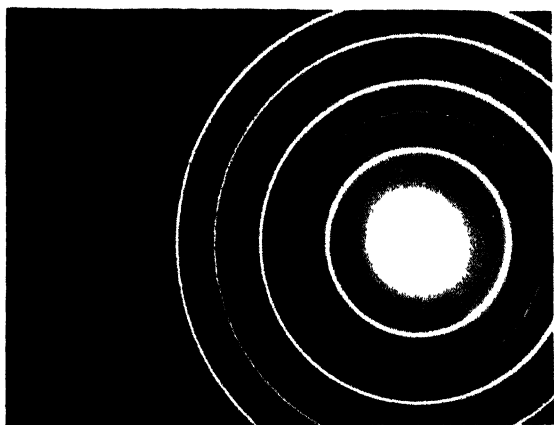


Fig. 81—Si—Cr el. dep. on Bi, normal pattern, very imperfect (111) orientation

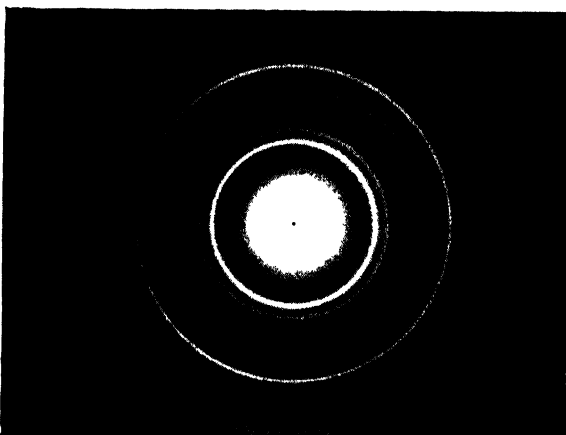


Fig. 82—Colloidal Au on collodion, inner ring due to collodion, (110) orientation.

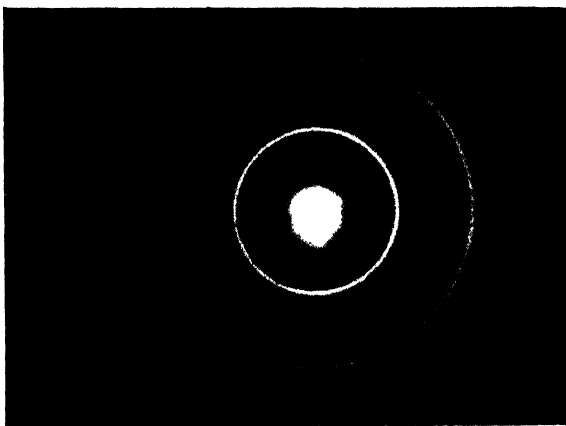


Fig. 83—Colloidal Au after removal from collodion support, normal pattern, (110) orientation.

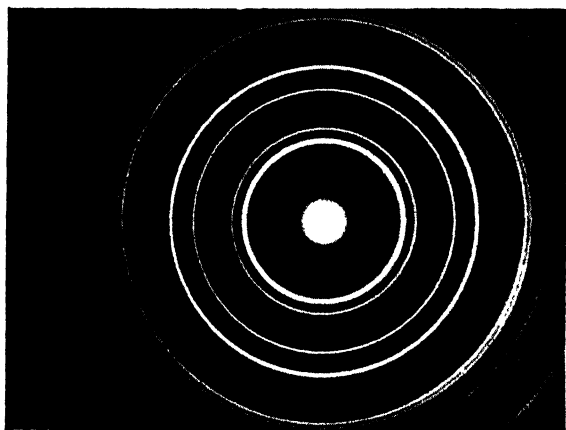


Fig. 84—Au el. dep. on Cu, normal pattern; (110) orientation.

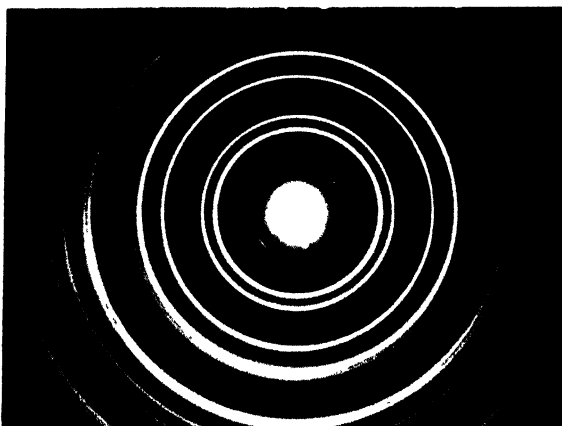


FIG 85—Au el dep on Cu, one very sharp extra ring

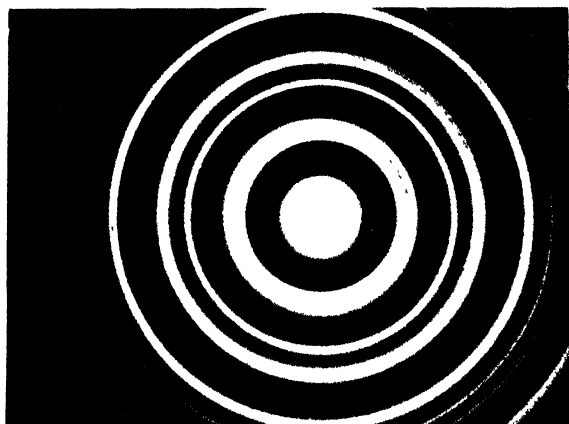


FIG 86—Au el dep on Sn, three "extra" rings, band from 200 ring to inside 111 ring, another band around central spot

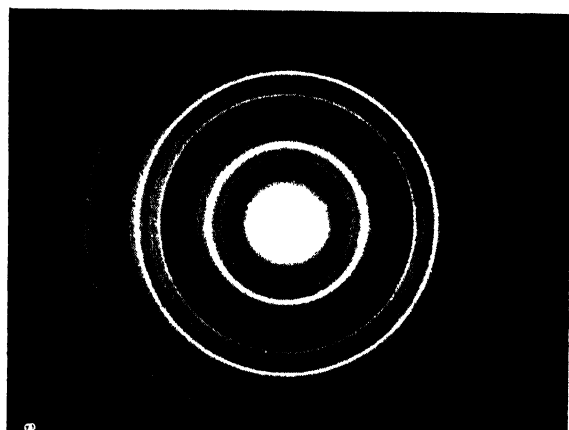


FIG 87—Au el dep on Bi, five well-developed bands and faint "extra" rings

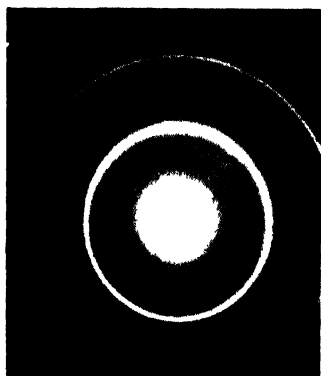


FIG. 88 - Wo el. dep. on Cu, faint diffuse "extra" ring

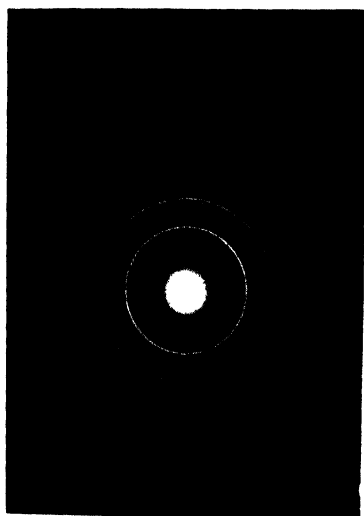


FIG. 89 - Sb el. dep. on Cu from Schluppe's salt solution

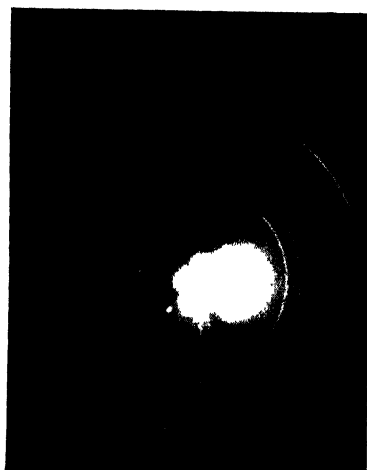


FIG. 90 - Cu el. dep. on Zn, normal pattern



FIG. 92 - Pt sputtered on quartz, (100), (111) and (112) orientations



FIG. 91. Au el. dep. on Cu; one "extra" ring, feeble (111) orientation

PLATE XXIX.



FIG. 1—Copper

See page 1104

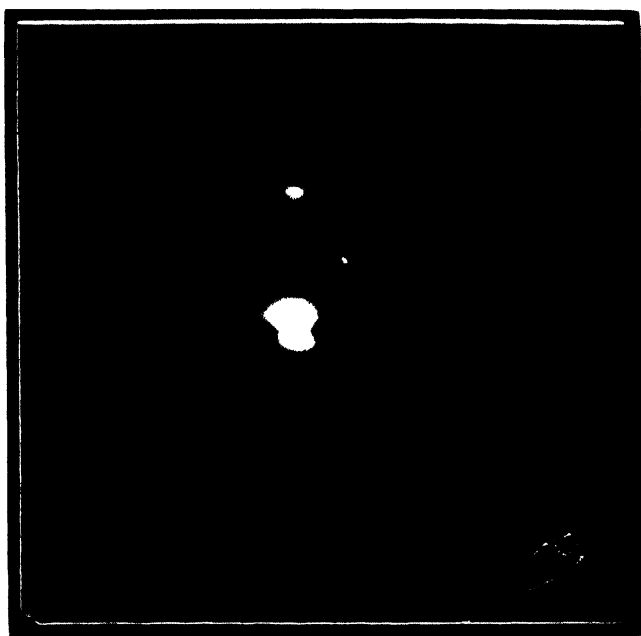


FIG. 2

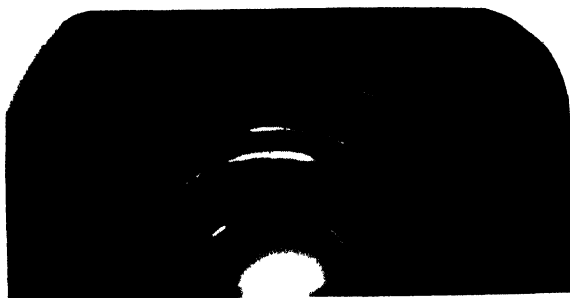


FIG. 3—Gold.

See page 1105.

PLATE XXX.

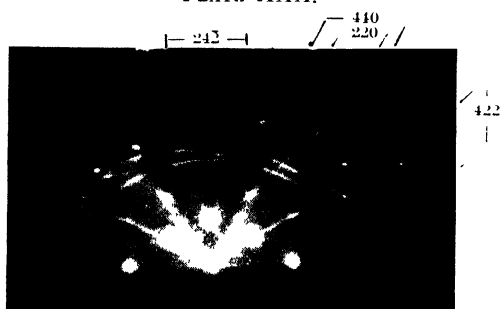


FIG. 1.

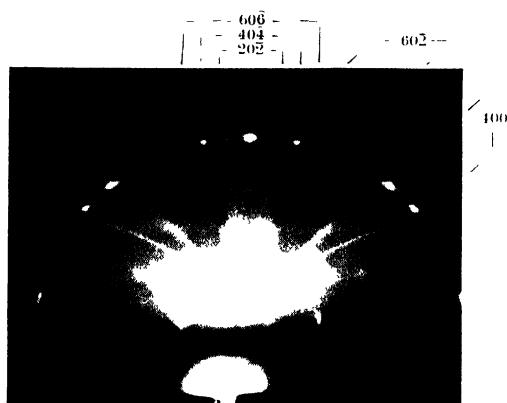


FIG. 2. [See page 1110.]

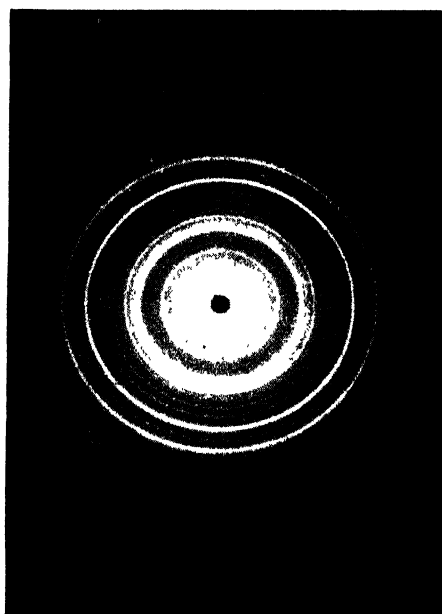


FIG. 3. [See page 1112.]

PLATE XXXI



FIG. 4

See page 1112



FIG. 5

See page 1113

PLATE XXXII.

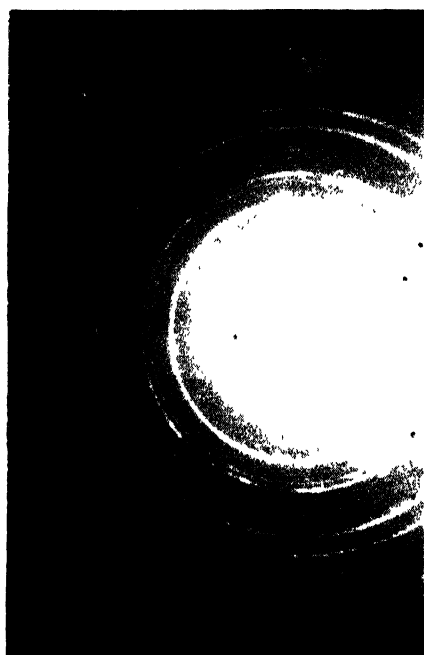


FIG. 7

[See page 1119.]

PLATE XXXIII.

TRIACEYL AND TRINITROCELLULOSE



FIG. 1 -- Rings

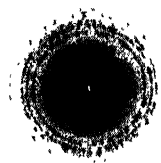


FIG. 2 -- Rings



FIG. 3 --Single crystal



FIG. 4 --Oblique incidence (50°).

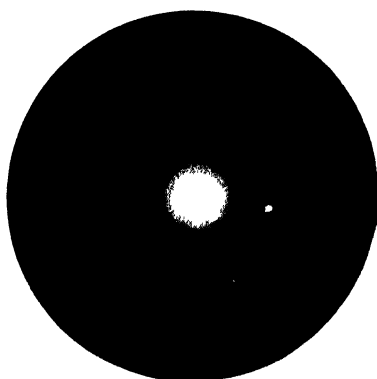


FIG. 5 --Nitrocellulose after irradiation for 15 minutes with electrons
(amorphous structure)

PLATE XXXIV.
NATURAL DEPOSITS ON METALLIC FILMS.

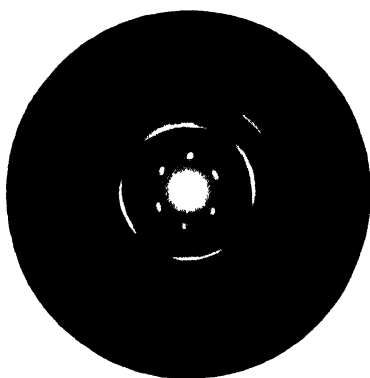


FIG. 6 —Beaten gold — Natural deposit

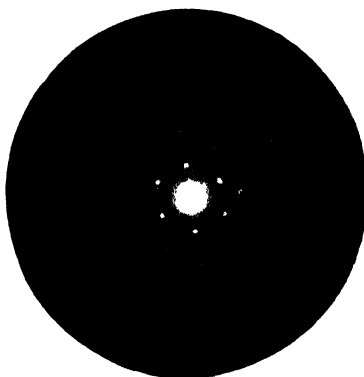


FIG. 7 —Ag — Natural deposit

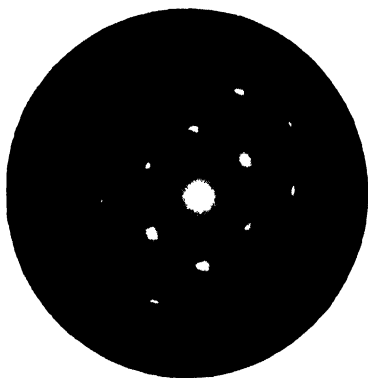


FIG. 8 —Pt (single crystal) — Natural deposit

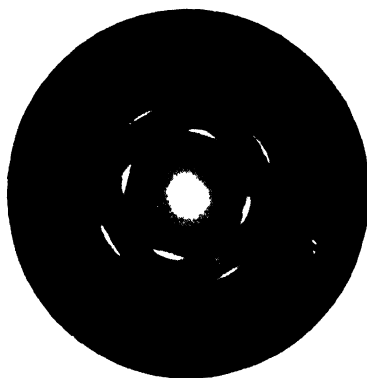


FIG. 9 —Beaten silver — Natural deposit



FIG. 10 —Gold — Natural deposit.

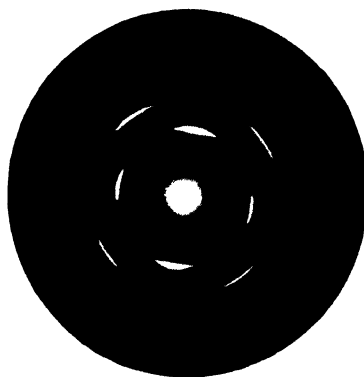


FIG. 11 —Pure gold — Normal diagram.

[See page 1129.

PLATE XXXV

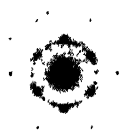


FIG. 12 Paraffin (single crystal)
Film obtained on water



FIG. 13 Stearic acid Film
obtained on water

ARTIFICIAL DEPOSITS OF THICK AND THIN LAYERS

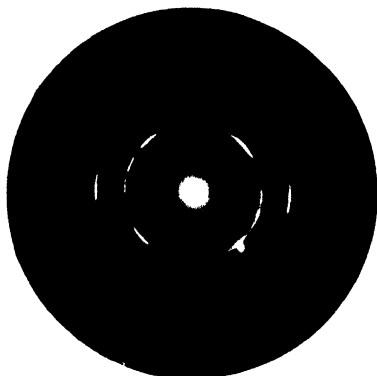


FIG. 14 Paraffin on gold (thin molecular
layer)

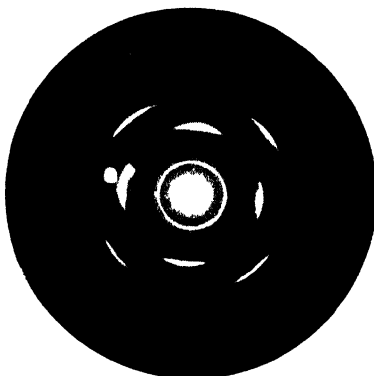


FIG. 15 - Paraffin on gold (15 or 20
molecular layer)



FIG. 16 Tristearine on gold (10-
molecular layer).



FIG. 17 - Beeswax on gold

[See page 1130]

PLATE XXXVI.



FIG. 1 ($\times 6000$)

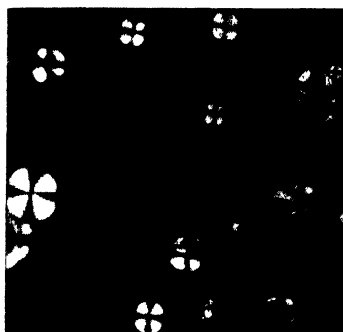


FIG. 2 ($\times 80$)

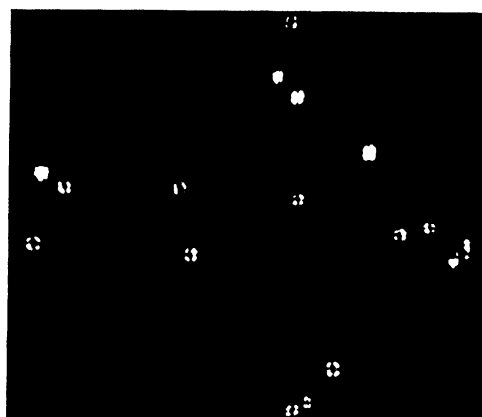


FIG. 3 ($\times 1000$)

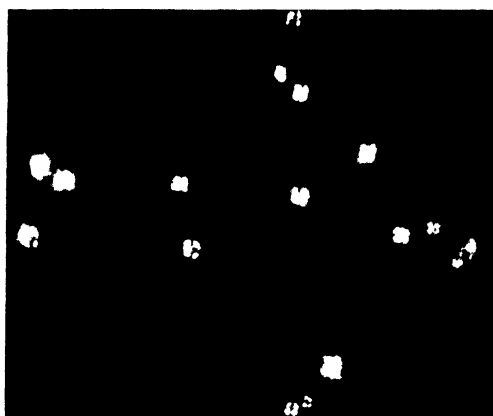


FIG. 4 ($\times 1000$)

See page 1139.

PLATE XXXVII

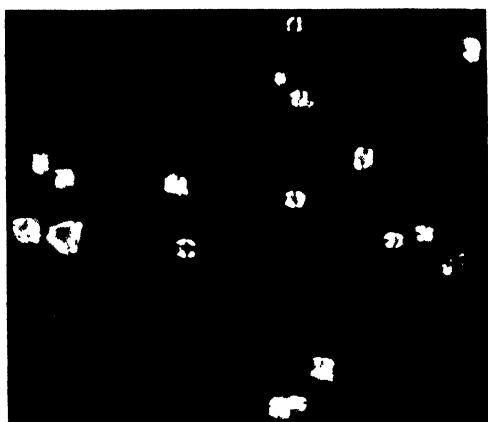


FIG. 5. ($\times 1000$)

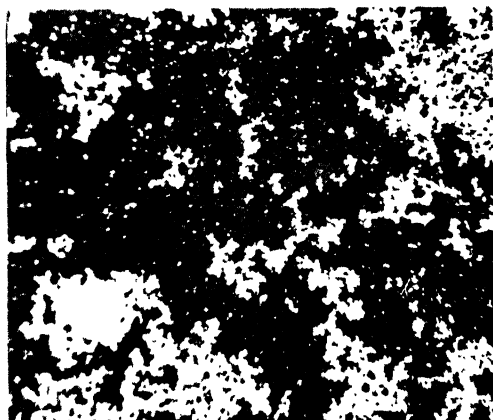


FIG. 6. ($\times 320$)

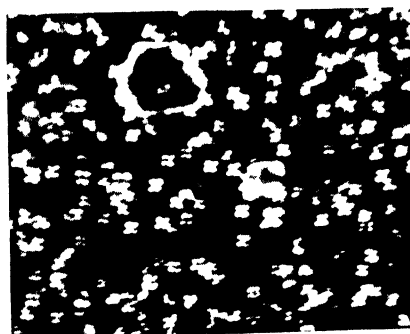


FIG. 7. ($\times 2000$)

(See page 1149.)

PLATE XXXVIII

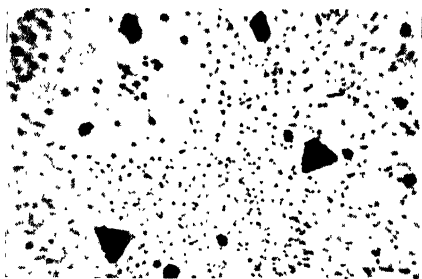


FIG. 8. (720)

[See page 1140]



FIG. 9. (720)

[See page 1142]

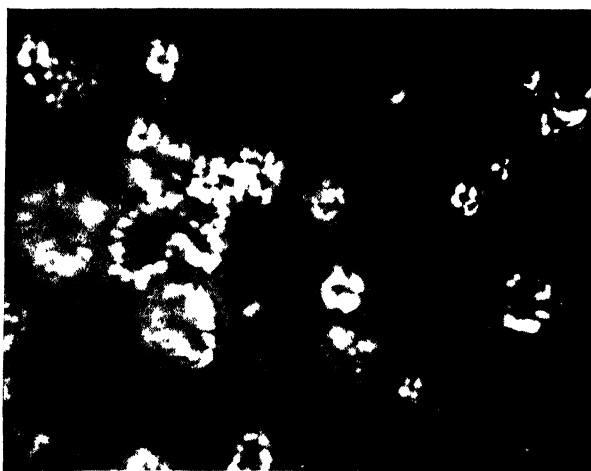


FIG. 10. (9500)

[See page 1142.]

PLATE XXXIX.

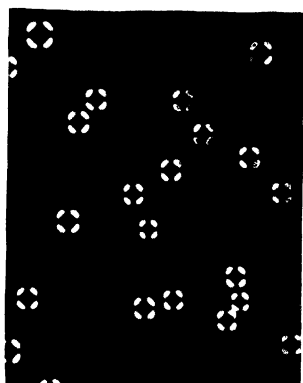
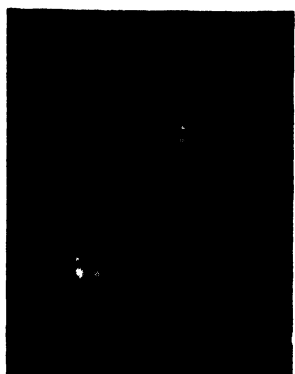


FIG. 1—Lead Sulphide ($\times 2000$). FIG. 2—Mercury drops, Diameter 3.4μ

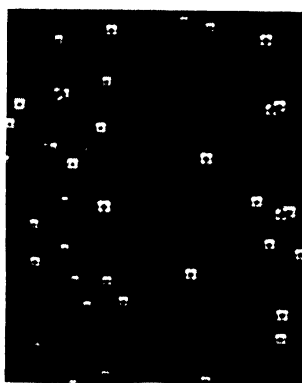


FIG. 3—($\times 10000$) Diameter 1.2μ

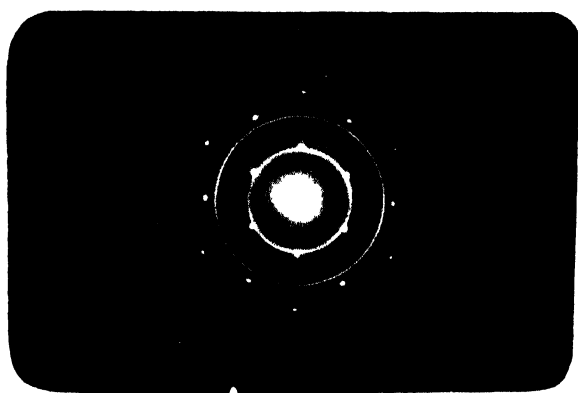


FIG. 4

(See page 1140)

PLATE XL

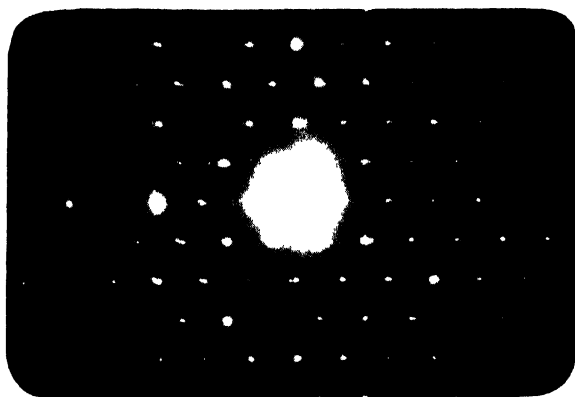


FIG. 7

[See page 1147]



FIG. 8.

[See page 1148]



FIG. 1 - Nickel deposit 0.012 mm thick, showing cracks giving relief of stress (75)



FIG. 2 - Nickel deposit, Brinell hardness No. 141 (75)



FIG. 3 - Nickel deposit, Brinell hardness No. 105 (75)
[See page 1170]

PLATE XII.



FIG. 4 - Nickel deposit, Brinell hardness No. 203. ($\times 75$)

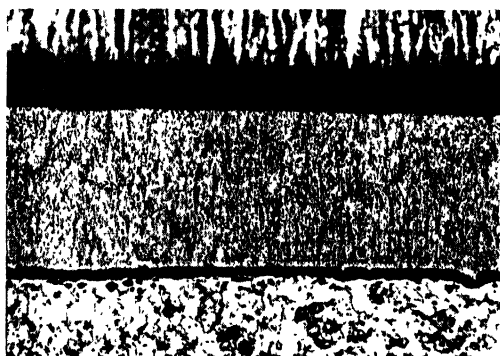


FIG. 5 - Nickel deposit, Brinell hardness No. 302. ($\times 75$)



FIG. 6 - Nickel deposit, Brinell hardness No. 418. ($\times 75$)

[See page 1170.

PLATE XLIII

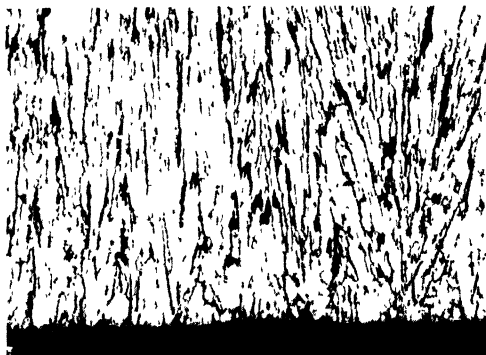


FIG. 8 Annealed nickel deposit showing non-metallic matter at grain boundaries.
 Binnell hardness number before annealing 156 (C 75)



FIG. 9 Annealed nickel deposit showing non-metallic matter at grain boundaries
 Binnell hardness number before annealing 223 (C 750)
[See page 1175]

PLATE XLIV



20 *a*



20 *b*

FIG. 1.



35 *a*



38 *b*

FIG. 2.



20 *a*

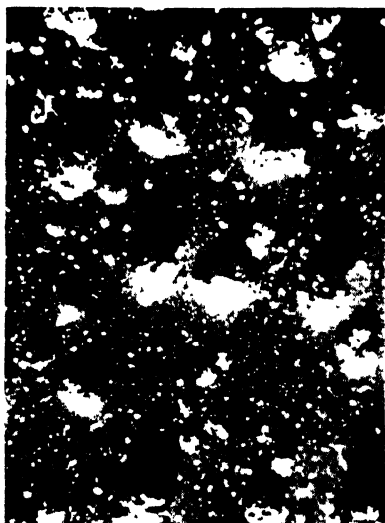


38 *b*

FIG. 3.

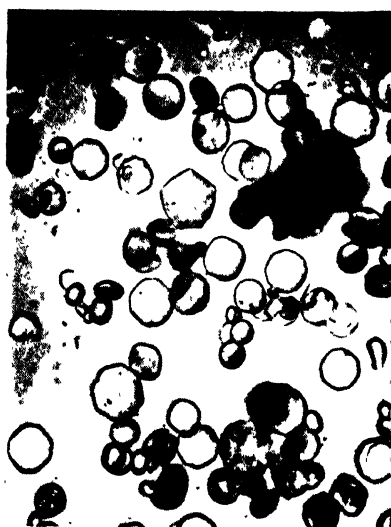
(See page 1187.)

PLATE XLV.



37

FIG. 4.

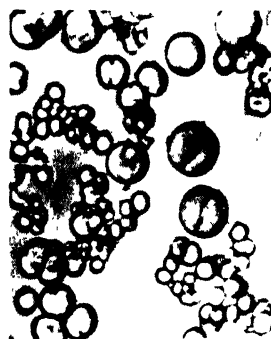


x 600

FIG. 5.



FIG. 6.



[See page 1187

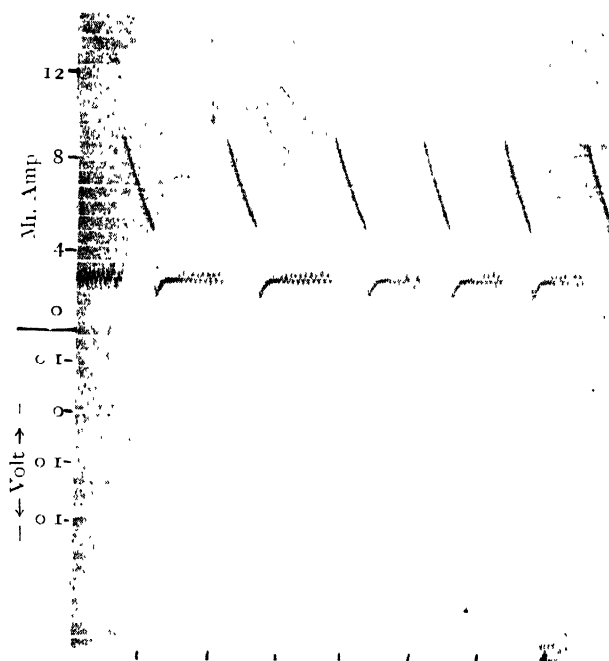


FIG. 5

(Abscissæ; time, one section $\frac{1}{4}$ sec., Ordinates: current density (heavy line); potential (thin line))

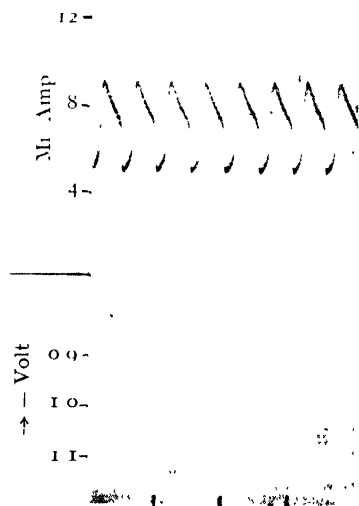
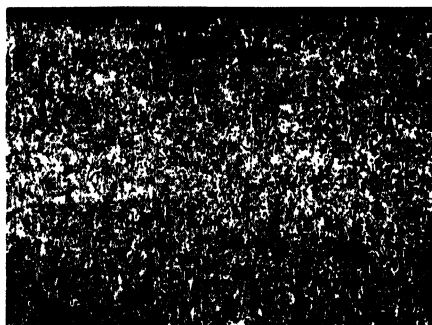


FIG. 6.

[See page 1199.]

PLATE XLVII

A

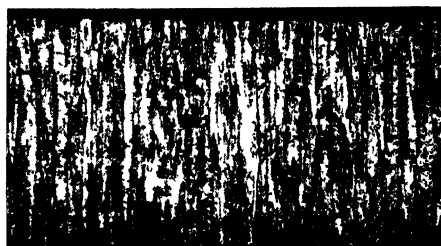


B



FIG. 1—Typical structure of deposits from nickel chloride solutions (Set 2)
A = $\times 100$ B = $\times 500$

A



B



FIG. 2—Typical structure of deposits from nickel sulphate solutions (Set 9.)
A = $\times 100$ B = $\times 500$

[See page 1209.

PLATE XLVIII



FIG. 3. - Typical surface and fracture of deposits from nickel chloride solutions
(Set 2.) $\times 5$

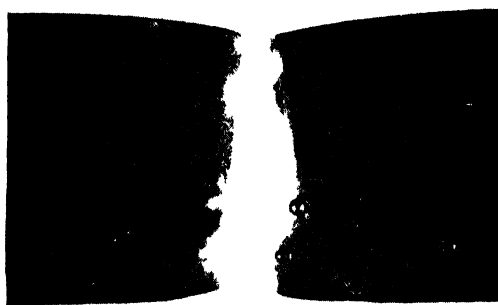


FIG. 4. - Typical surface and fracture of deposits from nickel sulphate solutions
(Set 10.) $\times 5$

[See page 1209.

PLATE XLIX.



FIG. 1 Deposit of chromium on steel

Bath CrO_3 300
 H_2SO_4 2
 Water 1000

Current Density 20 amps./dm²

1 hour at 35° C., then 17 hours at 67° C.

Shows growth of crystals normal to the surface of the cathode

Anodic attack in aqueous solution of 10 per cent CrO_3 (1000)



FIG. 2 Chromium on steel

Bath CrO_3 300
 H_2SO_4 2.7
 Water 1000

C.D. 20 amp./dm² Temperature 67° C.

Shows amplification, on the exterior surface, of a slight relief on the initial surface

Anodic attack in aqueous solution of 10 per cent CrO_3 (1000)

[See page 1212.]

PLATE L.



Fig. 3 -Chromium on steel.

Bath CrO_3 344
 H_2SO_4 174
 Water 1000

C.D. 53 amp /dm² Temperature 60

Cathode surface scoured, whilst current passing, in H_2SO_4 50° Bé. Shows the presence of inclusions of hydrates in the chromium and the fan-like development of crystallisation of this metal due to inclusion of hydrate. Anodic attack in aqueous solution of 10 per cent CrO_3 (100)

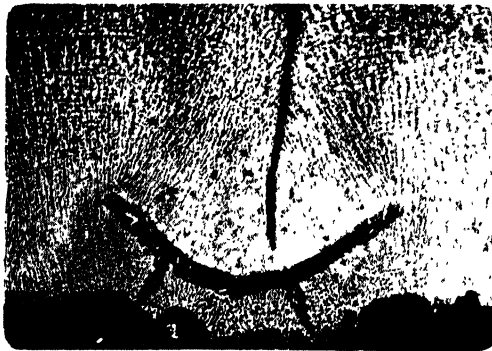


Fig. 4 -Nickel on steel

Inclusions of hydrate and convergent development of crystallisation, due to a spot of hydrate formed probably at a spot where there was a temporary bubble of gas adhering

Chloronitric attack (50 HCl + 50 NO_3H) at boiling point (300)

[See page 1212.

PLATE I.



FIG. 5. Nickel on steel—Influence of protuberances on the orientation of the crystalline structure of the deposit
Sulphomitic attack (50 HCl + 50 NO_3H) at boiling-point ($\times 100$)



FIGS. 6 and 7. Nickel on laminated and annealed nickel—Cathodic surface scoured before electrolysis in a boiling solution of ammonium persulphate—Influence of surface protuberances
Sulphomitic attack at boiling point—Fig. 6, $\times 100$, Fig. 7, $\times 300$.

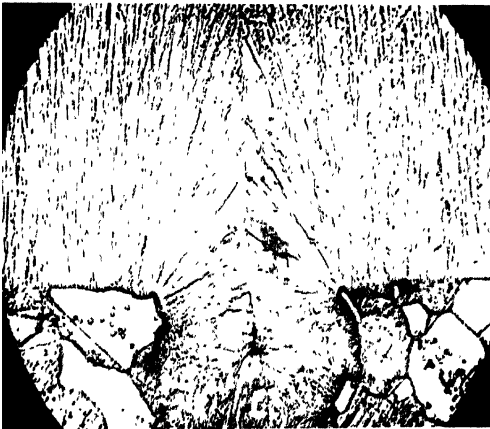
(See page 1213.)



FIG. 8 --Nickel on brass-- Influence of scratch produced in machining the surface --Inclusion of hydrate at junction of groups of crystals
Sulphonitric attack ($\times 200$)



FIG. 9 --Nickel on steel--Influence of irregularities of the surface on the orientation of crystalline groups
Sulphonitric attack ($\times 300$)



FIGS. 10 and 11 --Nickel on laminated, annealed and heavily scoured nickel-- Influence of cavities on the surface on the development and orientation of crystals

Boiling sulphonitric acid.

Fig. 10 - Cavity filled up by development of crystals ($\times 300$.)

Fig. 11 - Cavity not filled up by crystals, leaving a gap in the electro-deposit ($\times 1000$)

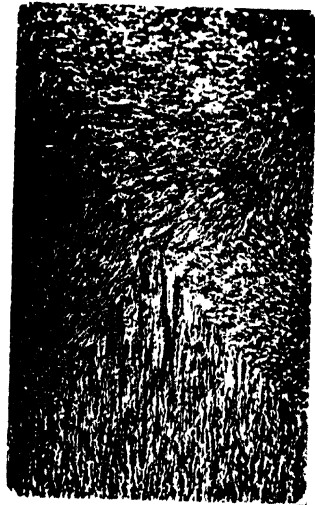
[See page 1213.]



FIG. 12 Deposit of nickel, showing a cavity resulting from the development of spherulitic crystalline groups.
Warm 30 per cent nitric acid



FIG. 13 Nickel on cemented tempered steel. Influence of a fissure (temper mark) on the structure of the deposit.
Sulphomitic attack { 200 }



FIGS. 14 and 15 Deposits of nickel, showing the junction of crystalline groups with convergent development, and interposed cavity (Fig. 14) or joined up (Fig. 15).
Boiling sulphomitic acid { 1000 }

See page 1213



FIG. 16—Nickel on grey phosphorous cast iron—Scouring of the surface of the support has left in relief the phosphorous eutectic of which the protuberances influence the crystalline structure of the deposit
Boiling sulphuric acid (× 1000)



FIG. 17—Nickel on grey cast iron, showing protuberances of graphite
1 per cent. nitric acid in alcohol (× 500)



FIG. 18—Fan-like electrodeposit of nickel starting from a bubble of gas.
Chloronic acid. (× 1000.)

[See page 1214.



FIG. 19



FIG. 20.



FIG. 21

FIGS. 19, 20 and 21. Electrodeposits of nickel on a cathode of laminated annealed nickel, showing the influence of the crystals of the base metal on the crystallisation of the deposit—amongst the crystals of the base, those which are clear after attack are continued by an equally clear crystalline sheath. The identity of crystalline orientation is thus proved by the absence of corrosion marks in the two cases.

Repeated attacks with boiling chloromtric acid ($\times 1000$)

{See page 1217



FIG. 22 - Nickel on laminated annealed nickel. The direction of crystallisation of the deposit orthogonal to the surface of the base crystals shows here that the effect of the geometric orientation of the surface influences the crystalline orientation of the metal.

Chloromitic attack (1000)



FIG. 23 - Nickel on laminated nickel. Here we see an orientation of the crystallisation of the deposit to the cathodic surface, showing that in this case the influence of the crystalline orientation of the base metal affects the geometric orientation of the surface.

Chloromitic attack. (300)

[See page 1217

PLATE LVII

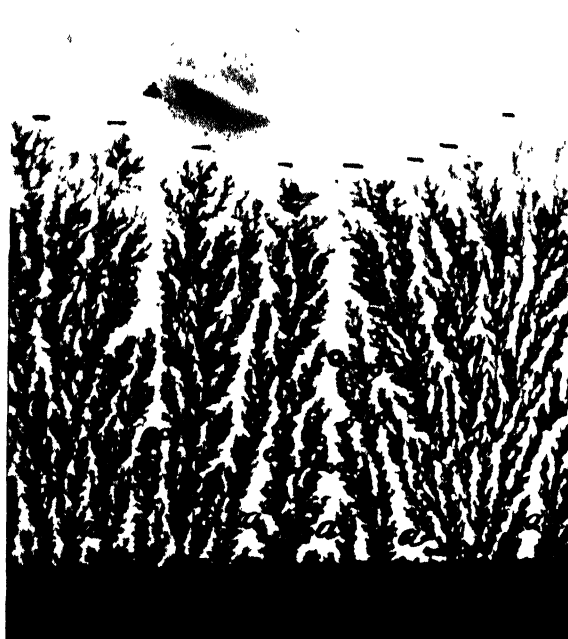


FIG. 2

Cathodic deposition of Ag from AgNO_3
The discharge will take place at the ends of the trees and
in the gaps & the trees do not grow

[See page 122.]



FIG. 4

[See page 1227]

PLATE LVIII.



FIG. 1.—Highly crystalline cadmium deposit obtained from electrolyte low in Cd and "free" cyanide content (Mag. 350.)



FIG. 2.—Deposit obtained from electrolyte high in Cd content (Cyanide electrolyte) (Mag. 350.)

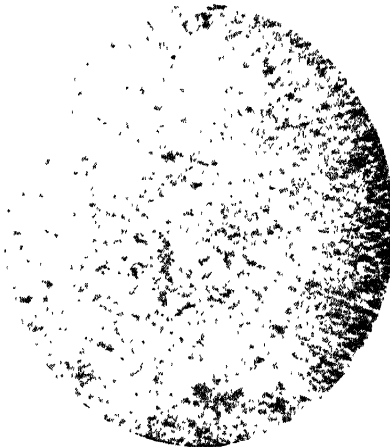


FIG. 3.—Deposit obtained from electrolyte high in Cd content, "free" cyanide and NaOH content (Mag. 350.)

(See page 1239)

PLATE LIN



FIG. 4 Cd deposit obtained from sulphate electrolyte, $p_{\text{H}} 3.0$ ($\times 350$)



FIG. 5 Cd deposit obtained from sulphate electrolyte, $p_{\text{H}} 4.3$ ($\times 350$)

See page 1240.

PLATE LX

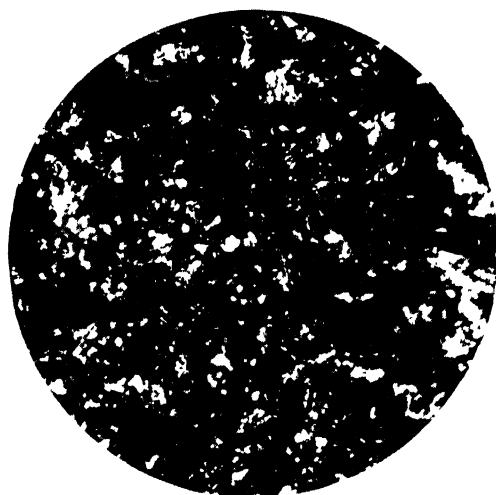


FIG. 6—Cd deposit obtained from sulphate electrolyte, p_{H} 5.0. ($\times 350$)

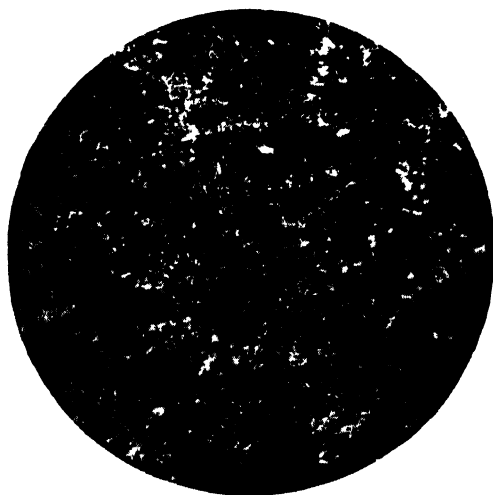
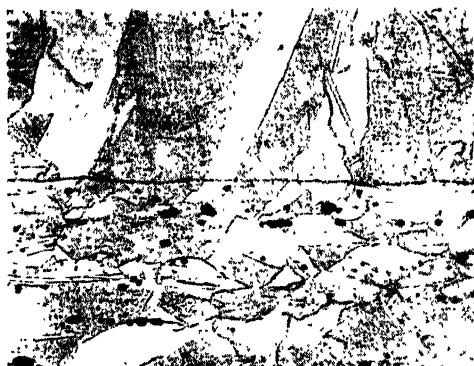


FIG. 7—Cd deposit obtained from sulphate electrolyte, p_{H} 5.3. ($\times 350$)

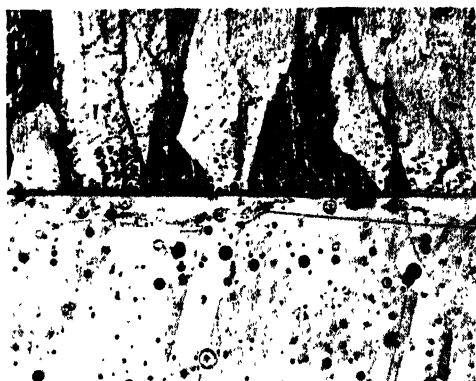
[See page 1240



Copper deposit.

Rolled copper.

FIG. 1—Electrodeposit of copper on rolled copper. ($\times 133$)



Copper deposit.

Nickel.

FIG. 2—Electrodeposit of copper on annealed nickel ($\times 66$) (The nickel surface near its junction with the copper is partially obscured by the film of varnish used in etching)



Copper deposit.

Silver.

FIG. 3—Electrodeposit of copper on annealed silver. ($\times 133$)

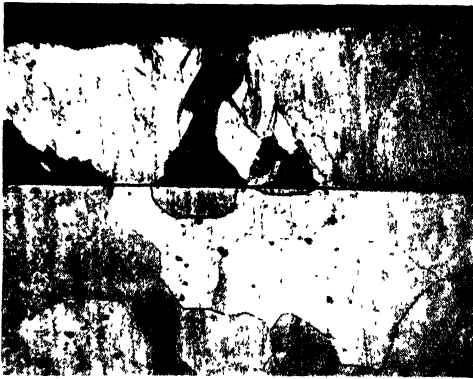
See page 1245.



Copper deposit

Brass.

FIG. 4 —Electrodeposit of copper on cast brass (2 per cent. Zn) ($\times 33$)



Copper deposit.

Brass.

FIG. 5 —Electrodeposit of copper on cast brass (10 per cent. Zn) ($\times 33$)



Copper deposit.

Brass.

FIG. 6.—Electrodeposit of copper on cast brass. (30 per cent Zn) ($\times 60$.)
[See page 1245.]

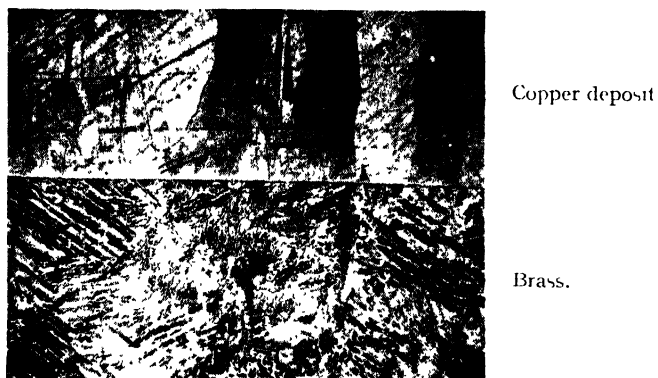


FIG. 7 —Electrodeposit of copper on cast brass (40 per cent Zn) (33)

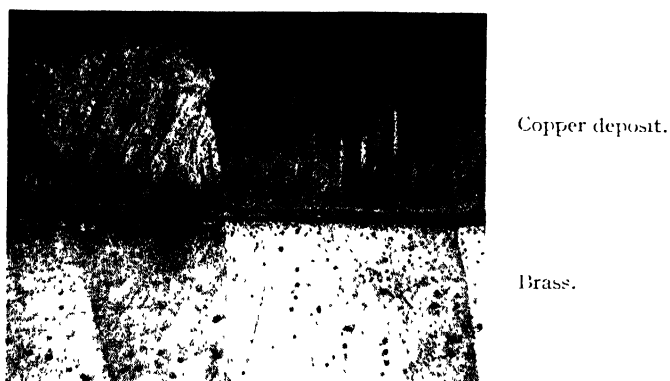


FIG. 8 — Electrodeposit of copper on cast brass (40 per cent Zn) (33)



FIG. 9 —Electrodeposit of nickel on annealed nickel (166)

(See page 1245)

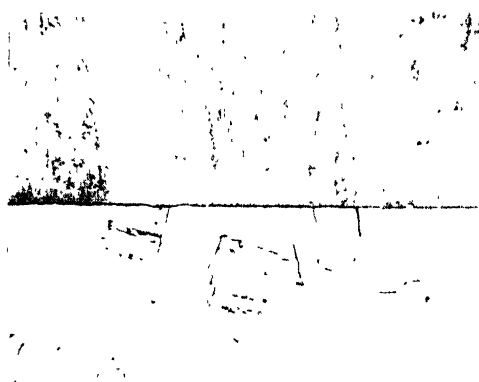
PLATE LXIV



2nd nickel deposit.

1st nickel deposit.

FIG. 10 -- Electrodeposit of nickel on filed nickel deposit ($\times 200$.)



Nickel deposit

Iron.

FIG. 11 -- Electrodeposit of nickel on annealed iron ($\times 60$)



Tin deposit

Cast tin

FIG. 12.—Electrodeposit of tin on cast tin ($\times 333$.)

[See page 1245

PLATE LXV.



Tin deposit

Annealed copper

FIG. 13 --Electrodeposit of tin on annealed copper (333)

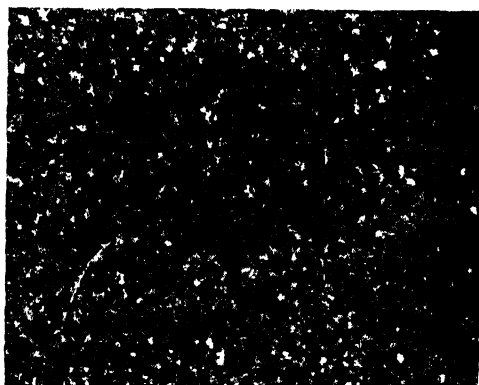


FIG. 14 --Surface appearance, as deposited, of nickel deposit 0.05 mm. thick, on annealed iron ($\times 22$)

[See page 1246.

PLATE LXVI.



FIG. 2.

[See page 1266.]



FIG. 5—Texture of sprayed nickel Unetched. Magnification 500

[See page 1271.]

PLATE LXVII



Fig. 6 - Texture of sprayed zinc - Unetched - Magnification 500.

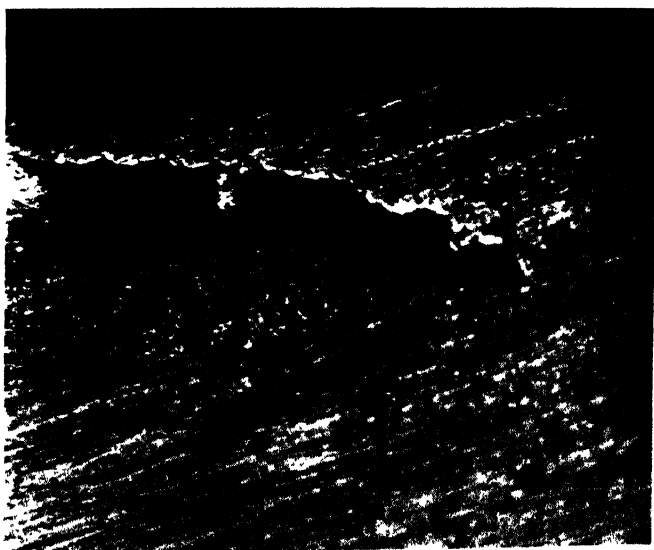


Fig. 7 - Aluminum sheet, sprayed with tin; unvarnished structure, loose contact between coating and base - Magnification 65

[See page 1271.

PLATE LXVIII



FIG. 10 —Pseudo-tight structure of sprayed nickel Unetched magnification 300

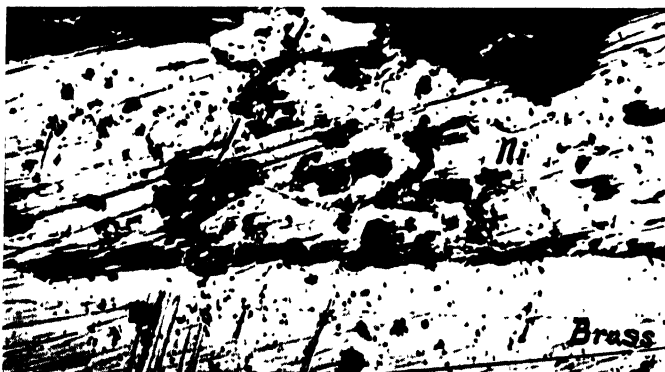
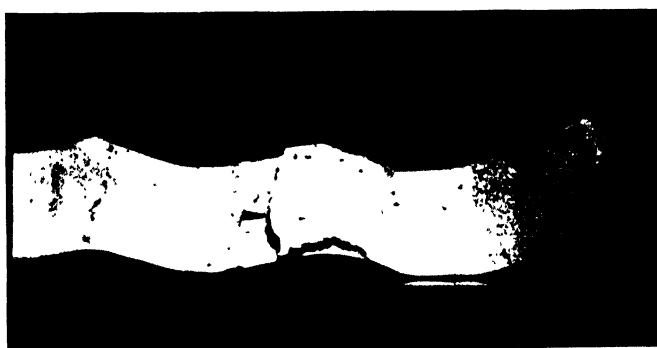
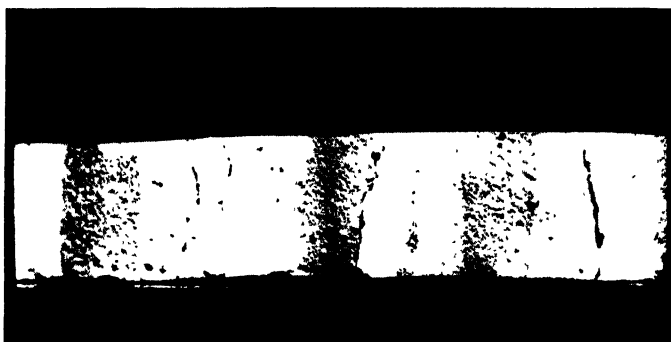
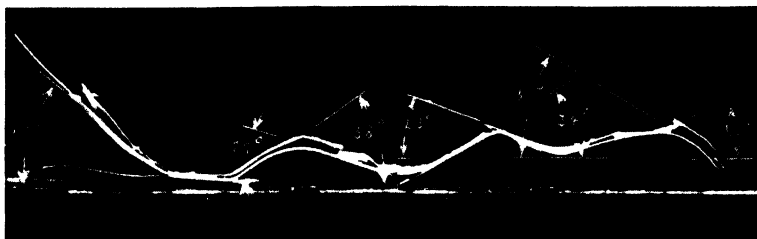


FIG. 12.- Structure of sprayed nickel, made really tight by use of an intermediate varnish-layer The dark patches which seem to be cavities are in truth capillary enclosures of varnish. Non-etched magnification 300

[See page 1273.

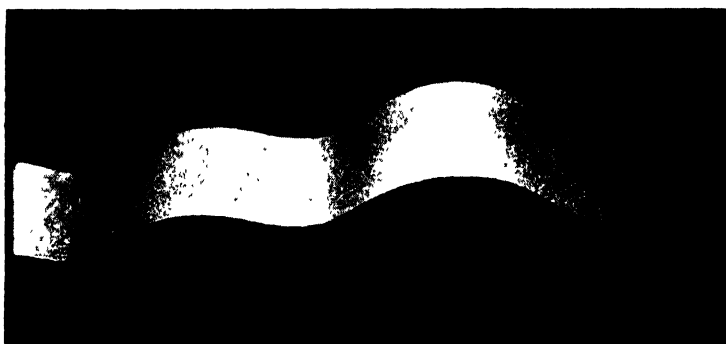
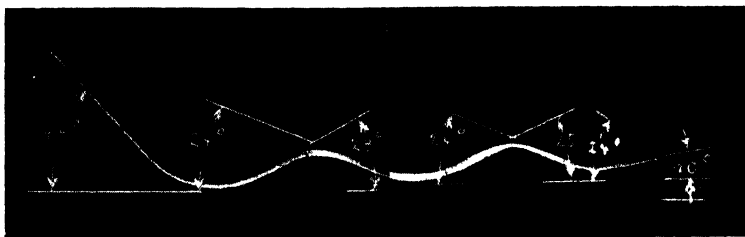
PLATE LXIX



FIGS. 13, 14, 15 --After one single bending through the angle shown in the drawing the sprayed nickel sheet has split off from the hard brass sheet (Natural size.)

[See page 1273

PLATE I.XX.



FIGS. 16, 17, 18 —After a single bending of the same kind as in Figs. 13-15 the sprayed nickel coating saturated with varnish shows no cracks or splitting-off (Natural size)

[See page 1273.]

PLATE LXXI.

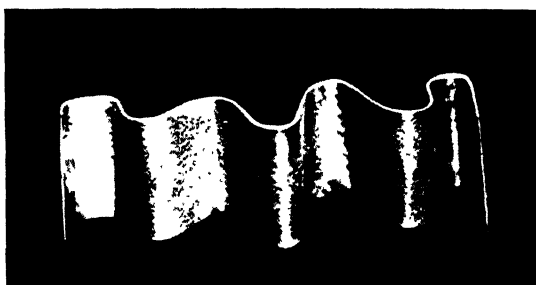


FIG. 19 —Brass strip, 0.5 mm. thick, with sprayed nickel-coating, impregnated with varnish. Bent through 180°. 1. 1.



FIG. 20 —Brass strip, 0.5 mm. thick, with sprayed nickel-coating, unvarnished. Bent through 180°. 1. 1.

[See page 1273.

PLATE LXXII.



FIG. 21.—Stretching experiments with a nickel-coated strip of brass sheet. The strip is fixed in the clamps of an Amsler machine (maximum load 10 tons, 500 kg. load steps).

[See page 1274.

PLATE LXXIII

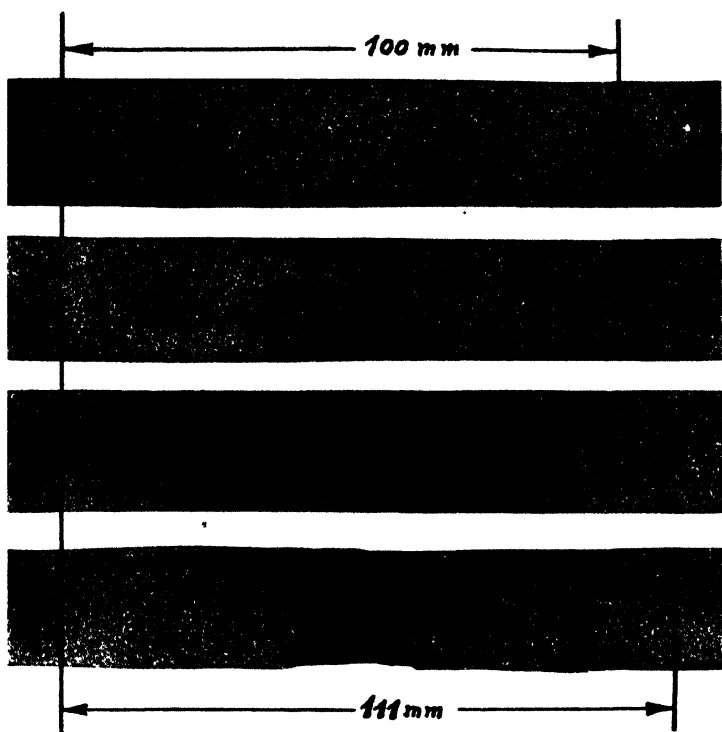


FIG. 22 Brass sheet, sprayed nickel coating (about 0.1 mm thick), without varnish

- (a) Sample before the experiment. Test-length, $l = 100$ mm
- (b) The limit of plasticity of the coating is attained, $l_1 = 105$ mm
- (c) Dislocations appear in the coating, test-length stretched to 105-107 mm.
- (d) The coating cracks and splits off (beginning at about 107 mm elongation and going on until the strip is torn in two at about 111-112 mm.)

[See page 1274.

PLATE LXXIV.

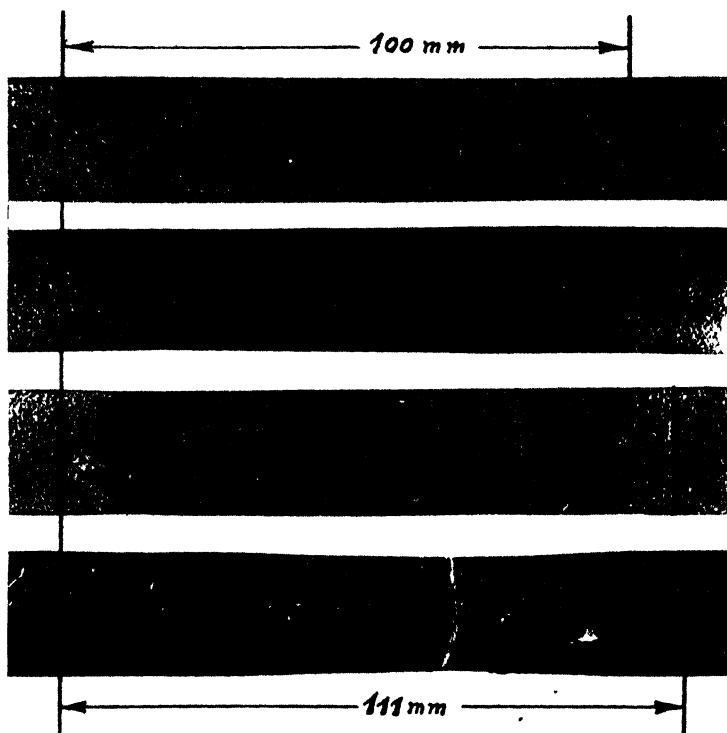


FIG. 23.—Brass sheet, sprayed nickel-coating (about 0.1 mm thick), varnished
 (a) Sample before the experiment. Test-length, $l = 100$ mm
 (b) Sample stretched to the limit of plasticity of the coating; $l_1 = 105$ mm.
 (c) Appearance of dislocations at $l = 105$ -107 mm
 (d) Cracking and splitting-off of the coating (beginning at $l = 107$ mm, and
 developing up to $l = 111$ -112 mm, the stretching limit of the brass sheet)

[See page 1274.

PLATE LXXV.

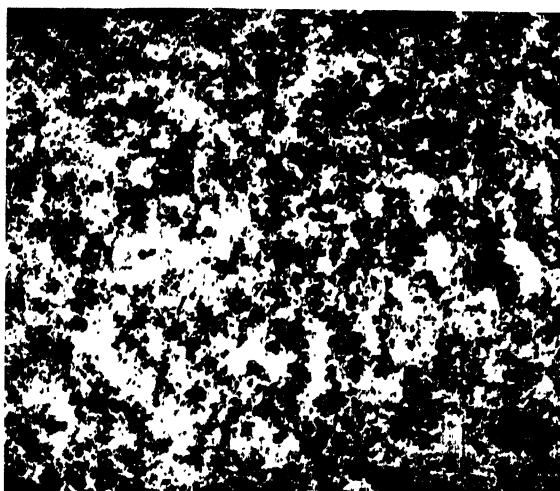


FIG. 24 — The rough edges of the lighter coloured metal particles and the great number of dark patches corresponding to grains which have been torn out are characteristic of the influence of grinding on unvarnished coatings.

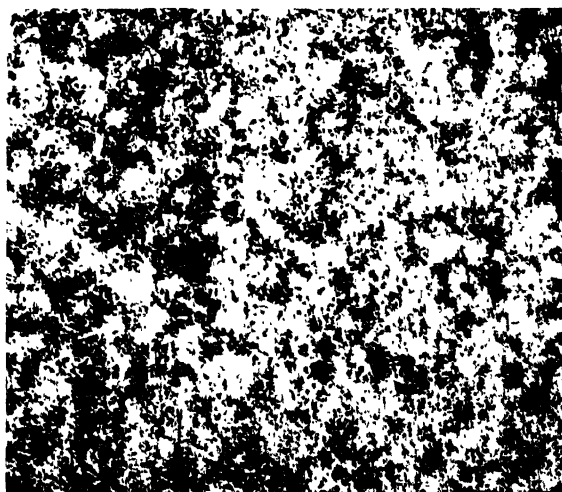


FIG. 25 — Unlike the surface shown in Fig. 24 the surface of a varnished coating has been preserved from the tearing-out of single grains during grinding by the protective action of the varnish. The structure has instead been "smeared over" and shows a bright metallic lustre, free from rough contours which are so conspicuous in Fig. 24.

[See page 1275

PLATE LXXVI.



FIG. 26 The remaining layer of the unvarnished coating splits off the base, well before the surface of the base has been reached by grinding.
Non-etched magnification, 10



FIG. 27 -- Impregnated coatings can be ground right down to the base without splitting off. This shows their better adhesion to the base
Non-etched magnification, 10.

[See page 1275.]



FIG. 2 —Cross section tin coating on copper $\times 800$. Etched ammoniacal cupric chloride followed by electrolyte etch in 10 per cent HCl



FIG. 3 —Tinplate detinned in dilute aqua regia $\times 15$ Shows "mottle"

See page 1280

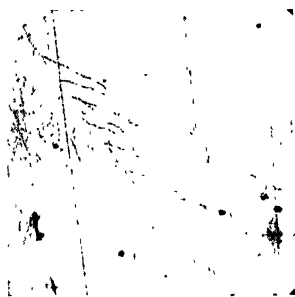


FIG. 5 —Unetched $\times 150$ Grain boundaries in tinplate

See page 1285



FIG. 1.

[See page 1287.

PASSIVITY OF GOLD.

By W. J. MÜLLER AND E. LÖW.

Received 12th April, 1935.

Some years ago one of us ¹ pointed out in this journal, that the time required for passivation of gold under different conditions, as measured by Shutt and Stirrup ² accords with that to be predicted from the theory known as "surface-layer-theory" (*Bedeckungstheorie*) of passivity. Meantime, Shutt and Walton, ³ as well as Armstrong, Himsworth and Butler ⁴ have published in this journal further investigations concerned with the same subject. The experiments were carried out either with electrodes freely suspended in the solution, or with strongly stirred electrodes. The following results were obtained: In very dilute hydrochloric acid a certain limiting current-density i_a is observed, below which no passivity can ever be obtained. With currents above the limit, a simple relation, of the form $(i - i_a)t = C$ exists between the current-density and the time required for passivation.

Shutt and his co-workers established, in a series of experiments that the passivity of gold, under the conditions prevailing in their experiments, is definitely due to the formation of a surface-layer of an oxide. If the current is switched off, this layer disappears during a so-called "time of recovery"—in the same way as is known to occur with the oxide layers of passive iron. In their recent work, the same authors found, using streaming electrolyte—which is practically equivalent to stirred electrodes—and a commutator permitting the interpolation of an interval of rest during the passage of the current—that the time which is necessary for re-activation becomes longer with *decreasing* concentration of the acid. There exists also a relation between the concentration and the time necessary for passivation: in this case, the time becomes longer with *increasing* concentration of Cl^- ions.

The authors give the following explanation of the effects observed. During the "active" period, an adsorption of Cl^- ions must take place as a preliminary step to the dissolution of gold. On a fresh metal surface, the velocity of adsorption is proportional to the concentration of Cl^- ions in the electrolyte. This velocity represents the maximum rate at which gold can be dissolved. In this way, the maximum current which can be carried by gold dissolving on the anode, becomes a function of the concentration of chlorine ions.

If this limiting current-density is exceeded, new phenomenon must occur at the anode. From their measurements of the potential-changes observed at this stage the authors suggested that the discharge of

¹ W. J. Müller, *Trans. Faraday Soc.*, 1932, **28**, 477.

² W. J. Shutt and V. S. Stirrup, *ibid.*, 1930, **26**, 635.

³ W. J. Shutt and A. Walton, *ibid.*, 1932, **28**, 741; 1933, **29**, 1210.

⁴ G. Armstrong, F. R. Himsworth, J. A. V. Butler, *ibid.*, 1934, **30**, 1143.

OH^- ions is a likely process. It leads to the formation of an oxide or peroxide layer. Armstrong is opposed to this conception. He and his co-workers think the phenomena under discussion must be connected with the consumption of depolarisators on non-attackable electrodes, a process which they have studied experimentally. One easily understands that this consumption proceeds more quickly when higher current-density is used.

From the point of view of our theory, we have some objections to the experiments described above. Reliable results concerning the time of passivation can only be obtained with *protected electrodes*, i.e., under conditions which exclude any convection, besides the inevitable diffusion and the transfer of the ions.⁵

If a freely hanging or a stirred anode is used, many of the metal ions dissolved are carried away by convection. The differential equation which applies to the case of a *protected electrode* is

$$dm = \delta dF = K(1 - u)idt \quad . \quad . \quad . \quad (1)$$

where dm denotes the amount of the salt deposited on the anode, during the time dt , δ the thickness of the layer formed, dF the surface covered, and i the current which has been flowing during the time dt . K is the electrochemical equivalent of the salt, and $(1 - u)$ its transference-number.

If the anode is unprotected, or stirred, the corresponding equation reads :

$$\delta dF = K(1 - u)idt - A dt \quad . \quad . \quad . \quad (2)$$

where A is the amount of the dissolved gold-salt which is carried away from the anodic layer of the electrolyte by convection during the time-interval dt . The amount of salt available for the formation of the passivating surface layer becomes smaller with increasing value of A , i.e., with stronger stirring. The limiting current-density, found by the above-mentioned authors, corresponds to the state, in which no saturation occurs in the anodic layer and the formation of a crystalline deposit on the anode becomes impossible. We have already shown this to be the case with iron-anodes.⁶ As soon as saturation of the electrolyte with the gold-salt actually takes place, a "primary" surface-layer is formed. As we have proved experimentally in many previous cases, the formation of such a layer changes the potential of the anode; it becomes nobler. We have called this effect a "surface-layer-polarisation."⁷ In this point our explanation differs from that proposed by Shutt and Walton, who explain the rise of the potential by a change in the nature of the process at the anode—i.e., an initial discharge of OH^- ions.

We will now describe some experiments which prove that the passivation of gold occurs according to the general laws formulated by us previously and based on the theory of passivation by formation of surface layers.

Using a cylindrical gold anode of 1 sq. cm. cross-section as a protected electrode,⁸ with 4 volts actual voltage, in a 5*N* HCl, and a platinum gauze cathode, we obtained the current-time diagram shown in Fig. 1.

⁵ W. J. Müller, "Die Bedeckungstheorie der Passivität der Metalle und ihre experimentelle Begründung." *Verh. Chemie.*, 1933.

⁶ Cf. note (5), p. 30.

⁷ W. J. Müller, *Monatshefte Chemie.*, 1929, **52**, 52; 1930, **56**, 461.

⁸ Cf. note (5), p. 103.

On placing the electrode under a reflection-polarisation-microscope,⁹ we observe the changes which are illustrated in Fig. 2. At first, the surface appears dark under crossed nicols (Fig. 2A). During the first five seconds of the passage of the current, the field quickly becomes brighter. This can only be explained by the assumption that a light-absorbing or reflecting surface-layer is destroyed by the current, and a strongly anisotropic metallic surface is laid bare. This result is highly unexpected, since gold is reputed to possess a regular lattice, and thus should by itself cause no polarisation at all. The explanation of the polarisation-effect actually observed will be given elsewhere and based on special experiments. For our actual problem, this effect is of no particular interest; in practice it was even favourable for the experiments.

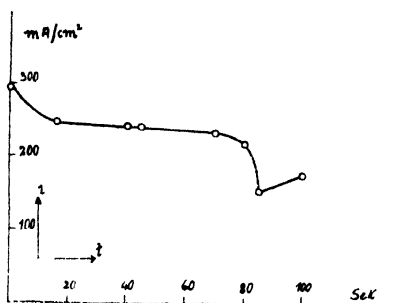


FIG. 1.

Shortly before the current falls to the low value characteristic of the passive state, we obtain under the microscope the picture shown in Fig. 2C—a diffuse layer of crystalline deposit. This layer is revealed even to the naked eye, by the strong glitter of the crystals. During the swift decrease of the current, this "primary" salt-deposit is transformed into a continuous, non-polarising layer, which completely covers the polarising surface of the gold. Illuminated with non-polarised light, the surface now appears uniformly bright, thus showing that the metal is covered with a strongly reflecting layer. The phenomena observed in 5*N.* HCl are thus completely in accord with the theory of passivation by surface-layers.¹⁰

During the "active" period gold is dissolved in the strictly tri-valent form, as demonstrated by the figures on Table I.

TABLE I.—DISSOLUTION OF GOLD IN 5*N.* HYDROCHLORIC ACID, TEMPERATURE 20° C

Voltage Applied.	Initial Current-Density Milliamps/sq cm	Final Current-Density.	Passivation Time Seconds.	Ag gr.	Au gr. Found.	Au gr Calc.
2	154	19	380	0.0362	0.0224	0.0228
2.5	185	36	315	0.0379	0.0217	0.0214
4	298	156	85	0.0247	0.0146	0.0151
6	362	260	21	0.0180	0.0046	0.0078

The amount of current passing through the cell was determined in the same way as in our previous experiments¹¹ by inserting a silver-coulometer in series with the cell. The amount of gold dissolved was calculated by weighing the anode before and after the passage of the current. The first column in Table I shows the applied voltage, the second the initial, and the third the final current-density in milli-amperes per sq cm. The fourth gives the times after which the passive state was attained, the fifth the weight of the silver-deposit, the sixth that of the gold dissolved. This is to be compared with the amount of gold calculated (in column 7) from the weight of the silver-deposit, on the assumption of a strict tri-valency of gold.

⁹ Cf. note (b), p. 18.¹⁰ Cf. ref. (b), p. 40.¹¹ W. J. Müller and E. Löw, *Z. Elektrochemie*, 1934, **40**, 570.

The occurrence of a surface-layer obscuring the polarising surface of gold metal, even before the beginning of the electrolyse, led us to an investigation of the behaviour of gold, which has been freed from this surface-layer by "etching" it in 5*N* hydrochloric acid. We etched an electrode, washed it quickly, first with distilled water, then with alcohol, dried it with a cloth, exposed it to air at room temperature and observed it under a polarising microscope, making repeated photographs with a constant time of exposure. The photographs are reproduced in Fig. 3 (1 to 8), they

clearly show a progressive darkening of the surface, which can only be explained by the formation of an oxide-layer under the influence of air.

All the prints reproduced in Fig. 3 were obtained with exactly the same exposure and on the same kind of paper.

The darkening of the surface, which is very pronounced, proceeds according to definite laws. We have

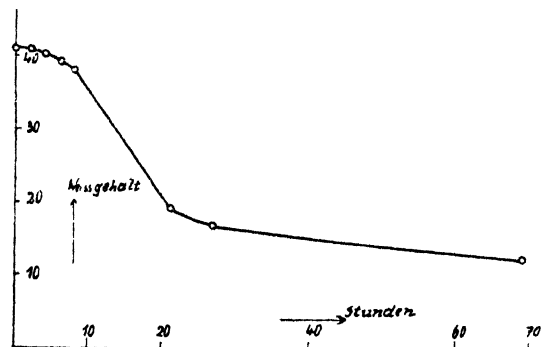


FIG. 4.

investigated them by leaving white, one and the same place on all the prints, and by measuring the relative darkness of the copies with a Pulfrich-photometer. The diagram given in Fig. 4 and showing the darkening as a function of time illustrates the regularity of the process.

The possibility must be discussed that the above effect may be due to a superficial change in the structure of the gold itself. (As mentioned above, no polarisation should be expected with a regular gold-lattice). This possibility is ruled out by experiments in which the passivity of gold

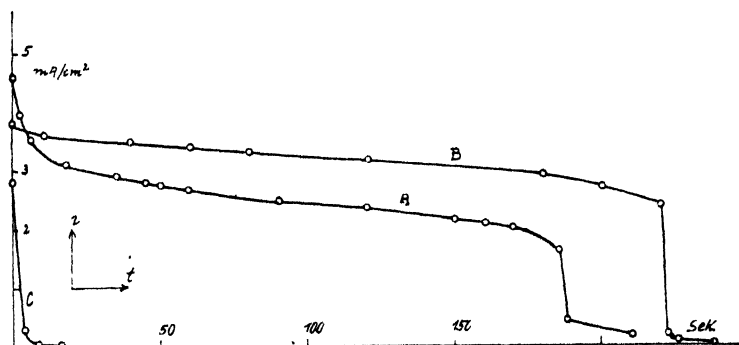


FIG. 5.

was studied in dilute (0.05 *N*.) hydrochloric acid. The conditions were analogous to these under which Shutt, Walton and Armstrong have worked, but protected electrodes were used. Fig. 5 shows the current as a function of time (curve A) and has been obtained with a freshly polished gold-electrode and a voltage equal to 1.5 volts. Curve (B) illustrates the behaviour of an electrode previously "etched" in 5*N*. acid, washed and dried quickly and then used in 0.05 *N*. acid. The mean current is now stronger than it was without etching, and the time required for passivation is longer (221 seconds instead of 187). Curve (C) shows the effects observed

1 2 3 4 5 6 7 8



FIG. 3

[See page 1294.]



FIG. 2.

[See page 1299.]



A B C D

FIG. 2

[See page 1293.]

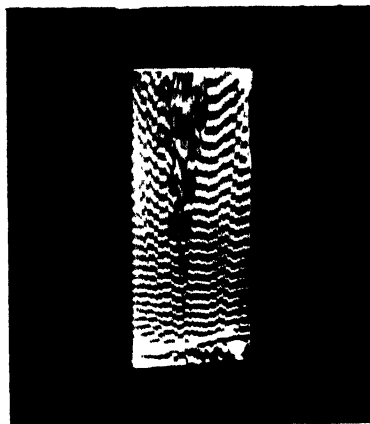


FIG. 1. [See page 1299]



FIG. 5



FIG. 6. [See page 1301.

with the same electrode, which, after etching, has been exposed to air for sixty-nine hours, and then used as an anode in 0.05 *N.* acid. Passivity is now attained in two seconds. Obviously a close insulating layer has been formed on the surface during the exposure to the air.

It must be mentioned, that Shutt and Walton¹² have already observed that gold electrodes which have been kept for some time exposed to the air, acquire passivity more quickly than electrodes with a freshly formed surface. They, too, explained this behaviour by assuming the formation of an oxide layer. Our experiments have proved the existence of this layer by direct optical evidence.

The experiments described above prove that gold, freed from its natural oxide layer, behaves as an anode exactly like other metals, as, for instance, iron. The laws of passivation by surface-layers are obeyed by gold in 5*N.* hydrochloric acid—because if this acid is used as electrolyte, the natural oxide layer is quickly destroyed by the current (in the same way as occurs with iron). In our experiments with iron, we have observed that in neutral electrolytes and in very dilute acids the oxide layer is not destroyed during the electrolysis, and that there-

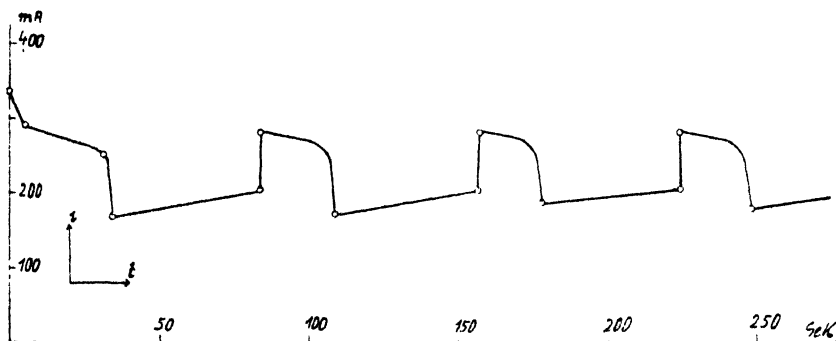


FIG. 6.

fore a much shorter time is required for passivation. This brought us¹³ to the assumption that a free metallic surface never occurs in these electrolytes.

We now proceed to the description of the experiments concerning the recovery-time of gold in hydrochloric acid of different strengths. Especially interesting are the results obtained with protected electrodes. In extended experiments with 5*N.* acid as electrolyte, and a potential of 5 volts, effects of the type shown in Fig. 6 were observed.

Immediately after the passivation, a brightening of the electrode can be recognised under the polarisation-microscope. During the forty-nine seconds after the passivation, chlorine is developed and the current rises slowly from 170 to 202 milliamps. Then, a sudden jump follows, and the electrode becomes active again. After twenty-three seconds, a re-passivation occurs, under circumstances described above and illustrated in Fig. 1. The change from the active to the passive state and back occurs again and again at regular intervals. We have observed up to eight repetitions of this process with one and the same electrode.

To explain these effects one is bound to assume that, even during the

¹² W. J. Shutt, A. Walton, *Trans. Faraday Soc.*, 1933, **29**, 1277.

¹³ W. J. Müller and D. Macher, *Z. physik. Chemie*, 1932, **161A**, 411.

passage of the anodic current, the oxide layer is slowly dissolved and ultimately destroyed. In measuring the current as a function of time, we find that after a very short interruption the electrode remains only a very short time in the active state. If the interruption-time is extended to five seconds, the time required for passivation is somewhat longer, sixteen seconds. The initial current is now 271 milliamps, smaller than when the electrode was first used. After an interruption for sixty seconds, the initial current is slightly higher (274 milliamps) and the time of passivation longer—twenty-three seconds, *i.e.*, the same period which is observed in non-interrupted experiments. If the interruption of the current lasts five minutes, the initial current increases to 320 milliamps, and the passivity returns after twenty-one seconds. These experiments prove that in 5*N.* hydrochloric acid the oxide layer is dissolved and the activity restored during interruptions as well as during the passage of the current. Both the time-intervals required for re-passivation and the initial currents observed after the return to the active state show that the oxide layer is destroyed by strong acid to a very high degree.

Different results are obtained in experiments with 1*N.* hydrochloric acid as electrolyte. In using an electrode etched previously in 5*N.* acid, and applying an EMF of 6 volts, we get the same initial current as above, but a passivation already after 3.3 seconds. If the current is allowed to flow continuously after passivation, no re-activation occurs in the course

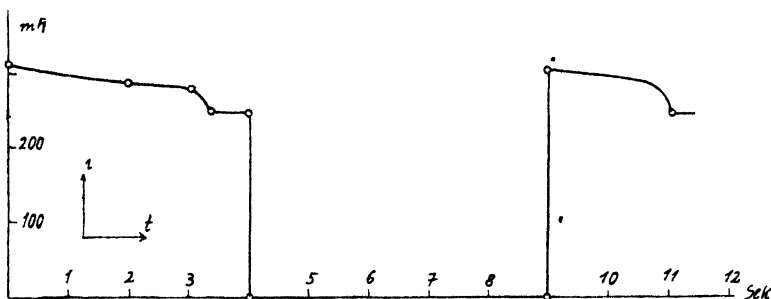


FIG. 7.

of ten minutes (as distinct from the results obtained in 5*N.* acid). Re-activation is actually observed after an interruption of the current for five seconds; but the time required for the electrode to become passive again is as short as 2.2 seconds.

With still more dilute acid (0.05*N.*) the amount of current transmitted is of course relatively small. If a potential of 2 volts is applied, the initial current is 19 milliamps. It decreases slowly to 11 milliamps in the next eleven seconds, and after twenty-two seconds the electrode becomes passive, the current dropping to 3 milliamps (Fig. 8). After an interruption of the current for five seconds, the current first increases although only to 7 milliamps, and after a further five seconds the residual value (3 milliamps) is again attained. This shows that the re-activation during the time of recovery (*i.e.*, the dissolution of the oxide layer formed in the course of the electrolysis) occurs in the dilute acid to a much lesser degree than in the more concentrated solutions, discussed above. This explains the results of Shutt and Walton, who found that the residual current (in experiments with stirred electrodes) is stronger with higher concentration of Cl^- ions, and the connected observation, that the time of passivation is longer in concentrated as compared with dilute acids.

The experiments described above, when compared with those of Shutt and Walton, and of Armstrong, clearly indicate that these authors

(it could hardly be expected to be otherwise) have worked with gold electrodes partly covered with oxide. The results which Shutt and Walton got in working with gold in a solution of sodium-chloride accord with this assumption. They found that a preliminary exposure to the air or to certain oxidising agents shortens the time of passivation; and they too explained this by assuming the formation of an oxide layer. On the other hand, their assumption that the oxide layer is destroyed even in dilute solutions is not in accordance with our results. Our experiments show that the total surface of the pores produced by the acid in the oxide coating of the metal grows with increasing concentration of the acid; only in 5*N.* acid does the destruction of the oxide become complete. The data communicated by Shutt and Walton concerning the time of recovery (which is nothing else than the time of dissolution of the oxide layer) accord with this assumption. They found it to be long in diluted acids and to become very short in 4*N.* acid.

Our experiments prove the existence of two kinds of oxide layers on gold. The natural layer is scarcely soluble at all in dilute acids; the

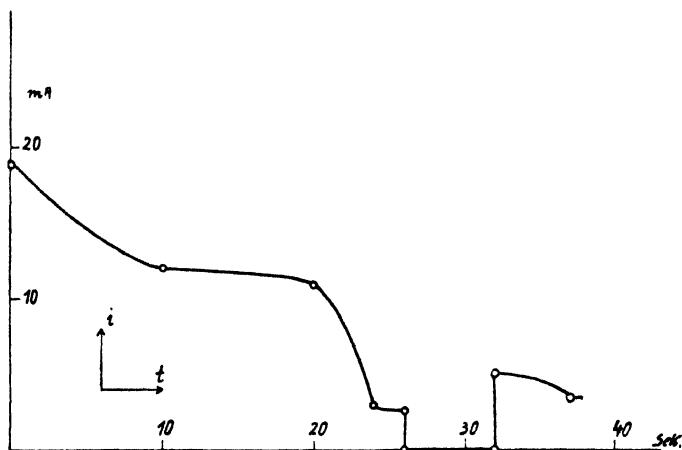


FIG. 8.

layer produced by chemical passivation is very unstable and to a great amount destroyed even by the weakest acids. By leaving the electrode for some time in dilute acid, the surface of the gold in the pores of the natural oxide-layer is again laid bare.

What must be the passivation-law in a case like this? The process of passivation consists (with an anode of this type) in a crystallisation of the metallic salt in the pores of the natural oxide-layer. This crystallisation takes place until the current-density reaches the value corresponding to the $1/i^2$ law. Unlike the case of free metallic surfaces, one may in this case, expect the thickness of the deposit to depend chiefly upon the thickness of the existing oxide layer. The dependence of the thickness of the deposit on current-density, as expressed in the $i_0 t^2$ -law, cannot be expected to hold here, since the amount of salt formed is given by the formula

$$m' = \delta F = K(1 - n)it \quad . \quad . \quad . \quad (4)$$

and the law $it = \text{Constant}$ must be obeyed in this case.

If one uses a suspended or, still more, a rapidly-moving electrode, no surface layer will be formed at all until a certain current-density is attained, because a great number of ions is removed by convection. If we deduce this number from the total current passed, we obtain the law which has been found to be valid by Shutt and Walton as well as by Armstrong, *viz.*

$$(i - i_a)t = \text{const.} \quad . \quad . \quad . \quad (3)$$

It thus appears possible to explain all the facts found by Shutt and Walton and by Armstrong from the point of view of the theory of "passivation by surface-layers."

Summary.

Experiments with 5*N.* hydrochloric acid as electrolyte have shown, that in this case the passivation of gold occurs according to the laws of passivation by surface-layers and chemical passivation as formulated by us previously.

It was found that gold exposed to air becomes coated with an oxide-layer, which is removed during passivation in concentrated acid. The surface freed in this way from the oxide is re-oxidised if left in contact with the air.

In analogy to the behaviour of iron in very dilute acids, it was found that the oxide-layer of gold is not destroyed by anodic current in dilute hydrochloric acid. The anodic passivation remains limited in this case to the pores of the natural oxide layer. The relation between initial current and time of passivation is in this case

$$(i - i_a)t = \text{Const.}$$

in accordance with the experimental results of Shutt, and Walton and of Armstrong.

The differences in the behaviour of the protected and of freely suspended electrodes are of a quantitative nature only. With a protected electrode, the passivity will be attained sooner or later, even with the smallest current-density. (Iron in sulphuric acid, with an initial current-density of 18 milliamps per sq. cm. became passive first after twenty-two hours). With electrodes freely suspended or stirred, the time of passivation is much longer and there exists, as observed by Shutt, Walton and Armstrong, a lower limit of the current below which no passivation occurs at all. This is explained as due to the fact that dissolved metal is carried away from the anode by convection; no super-saturation and following crystallisation can take place near the anode under these conditions. The observation that the limiting current is higher if the stirring is stronger (other conditions being unchanged) is in accordance with the predictions of the theory.

The experiments make very probable a difference in the character of the natural oxide-layer formed on gold surfaces exposed to the air, and the "secondary" layer produced by electrolysis. The natural oxide coating is somewhat stable and dissolves only in a strong (5*N.*) hydrochloric acid. The secondary layer produced during the anodic passivation is much less stable and disappears quickly even in very dilute acids as soon as the current has been switched off.

The investigation of the protected gold anodes from the point of view of their "recovery" in hydrochloric acid of different concentrations showed, that in 5*N.* acid the secondary oxide layer, which is responsible for the passivation, is dissolved to a certain degree even during the passage of the current. The alternative formation and dissolution of the oxide layer leads to regular long-period oscillations of the current-density.

In sufficiently diluted acids (1*N* and 0.05*N*.) no dissolution occurs during the passage of the current. The time of passivation of a re-activated electrode is the shorter the less concentrated the acid.

All these results show that there is no reason to see in the anodic behaviour of gold any anomalies from the point of view of the theory of passivation by surface-layers, has been developed by us previously. This theory has been found to accord with the experiments in the cases of all metals so far thoroughly investigated.

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STRIATIONS IN TIN COATINGS ON COPPER.*

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Fig. 1 is a photograph—natural size—of a slip of cathode copper which has been tinned by hot-dipping. The specimen has not been etched or treated in any manner, the photograph being taken directly after tinning of the tin surface itself. It will be seen to present an unusual appearance—an appearance which will be designated here as the “Eutectic pattern” of tin coatings on copper. This pattern has been much exaggerated in the photograph, by means of suitable lighting, but it is nevertheless obvious and striking in the specimen itself. The appearance of a surface such as that represented in Fig. 1 can be described, from a physical point of view, as consisting of a smooth, normally reflecting surface, crossed by regions which scatter or diffuse the light falling on them. In the photograph, which was taken with oblique illumination, the dark parts are those in which the light is reflected normally, and so does not reach the camera; the bright parts are the regions in which reflection is irregular, some of the light consequently being received by the camera.

The striations appear at right angles to the direction of crystallisation. The specimen in Fig. 1 was cooled from the top downwards. This typical pattern is best obtained when crystallisation occurs uniformly in one direction across an inch or two of the specimen. The structure is still distinct but less obvious when crystallisation does not take place uniformly. It is then seen as concentric striations radiating from the nucleus of crystallisation. As most commercially tinned copper articles are cooled irregularly or quenched, it is understandable that the pattern has not previously attracted attention.

Optical and Micro-Examination.

Examination under the microscope with low powers indicates that the visual appearance of the pattern is due to alternating areas of tin with smooth, and mottled or cellular surfaces, the cells appearing as a sub-structure within the crystal boundaries. Fig. 2, magnification 100, shows two crystal boundaries (vertical) with the cellular structure in various

* Communication from The Sir John Cass Technical Institute, Aldgate, E.C.3.

amounts between them. Higher magnifications reveal nothing more unless the specimen is etched. Etching with either ferric chloride or hydrochloric acid greatly enhances the pattern, the effect being to reduce, and finally completely to suppress, the regular normal reflection of the surface. Each element of the surface then reflects as if it were inclined to the general surface of the specimen, the appearance being that of a series of shallow transverse depressions. The reflection of light takes place as from a series of concave reflecting surfaces, the point of reflection varying according to the direction of the incident light. The surface of the specimen still appears to be crossed by a series of bright striations spaced as before but the actual position of the striations depends on the illumination.

This apparent undulation of the surface was investigated more fully by examining the specimen under a low-power microscope ($\times 15$) fitted with an eyepiece scale. Illumination was obtained from a single lamp, the position of which could be varied as required. The specimen was so placed that two bright striations could be seen simultaneously, and their positions on the eyepiece scale observed.

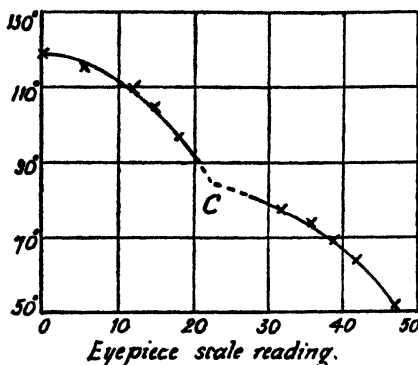


FIG. 3.

men (*i.e.*, a plane perpendicular to the striations). Observations were made relating the position of the bright striations with the angle between the incident light and the horizontal. From this was deduced the angle of the effective optical normal at each point, and a graph relating position and inclination of the optical normal is shown in Fig. 3.

By starting from the central point C, where the optical normal is perpendicular to the surface, and integrating the slope of the curve, the profile of a continuous surface that would give the observed effect can be calculated. The result of such a process is shown in Fig. 4, which shows the height of any point above the level of the point C plotted against the eyepiece scale reading of that point.

The extreme depth indicated by this curve is nearly 0.2 mm., which indicates that a surface giving rise to the observed effect as a result of ordinary surface reflections must have variations of depth of this order of size. Microscopic observation, and the fact that a partially etched specimen shows some reflection corresponding to a plane surface as well as the reflection described above, indicate that actual changes of depth are far less than 0.2 mm. Hence the effect described cannot be due to undulations brought about by etching.

Microscopic examination with higher powers indicates that the inclined reflections from a deeply etched surface are from etch-facets that are inclined to the surface in a periodically varying manner; this periodic variation of the inclination of the facets takes place within the single crystals of tin. The etch-facets, although just visible under the microscope, are too small to be photographed.

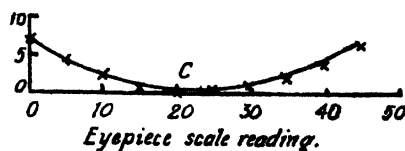


FIG. 4.

With lighter etching (with concentrated hydrochloric acid), a difference is visible under high powers between the different parts of the surface. Fig. 5 ($\times 1500$ diameters) shows an area consisting entirely of eutectic, while Fig. 6 shows an area containing little or no copper. The photographs were only obtained with difficulty, due not only to the extreme fineness of the eutectic but also to the difference of level caused by etching.

With prolonged etching the area of eutectic increases to the point where all distinction between the various bands is lost under higher magnification, the surface then consisting of the etch-facets mentioned above.

It is of interest at this stage to investigate the nature of the material of which the reflecting facets are composed; the only two phases that can be present are tin and the intermetallic compound CuSn , and by using Drude's polarised light method it is possible to choose between these two possibilities. According to Drude's theory of metallic reflection, when circularly polarised light falls on a metallic reflector, it is reflected as elliptically polarised light. At a particular angle of incidence, this becomes plane polarised, and the angle of incidence and the plane of polarisation both depend on the optical characteristics of the reflector. For a discussion of similar applications of Drude's theory of metallic reflection see¹.

In order to apply this, circularly polarised monochromatic light was allowed to fall on various surfaces at a definite angle of incidence, and the setting of an analysing Nicol prism for best extinction was obtained. It was found that when tin surfaces that had been treated in various ways (*i.e.*, polished, etched, etc.) were used, the setting of the analyser was always the same within two degrees. A surface of CuSn , obtained from a specimen of tinned copper by electrolytic removal of the tin layer, was found to give a setting differing by 20° from that of tin. Light reflected from both the unetched and etched "eutectic pattern" specimens gave settings within the range associated with pure tin. Hence the irregular reflections of the unetched specimen and the abnormal reflections of the etched specimen are definitely identified as reflections from tin and not from CuSn .

Conditions of Formation.

The principal facts governing the production of the "eutectic pattern" can be summarised as follows:—

1. The copper slip, before tinning, should be fairly smooth. A high polish, although desirable, is not necessary, and the pattern can still be obtained even following upon rubbing with emery.

2. The copper should be thoroughly degreased and adequately fluxed. The pattern is not obtained if there is not a satisfactory wetting of the copper by the tin. This is in effect stating that a reaction between the copper and the tin must occur. Good fluxes show the pattern better than less satisfactory fluxes, stannic bromide being better in this respect than zinc chloride. The specimens examined in this work were polished with "Silvo," degreased in the vapour of trichlorethylene, and fluxed with stannic bromide which had been dried on the surface of the copper before immersion. No additional flux was used on the surface of the tin bath.

3. The structure is not sensitive to changes in temperature of the tin bath, but as the coating tends to become irregular in thickness at temperatures higher than 270°C. , the specimens studied were dipped at about 260°C.

4. The spacing of the striations is sensitive to rate of crystallisation. The striations become more widely separated the slower the rate of cooling.

5. The pattern does not depend upon movement of the tin when still molten. With the specimen held vertically so that the tin runs downwards forming a drip at the bottom, crystallisation can be made to occur upwards by maintaining the top of the specimen hot. The pattern in this case is unchanged.

¹ L. Tronstad, *Trans. Farad. Soc.* This vol., p. 1151.

6. The pattern is not sensitive to normal changes in the copper content of the tin bath. If anything, the clearest patterns are obtained with pure tin. Chempur tin was used in these experiments.

Copper Content of Coating.

A number of specimens were carefully tinned in Chempur tin, taking every precaution to secure continuous coatings and an absence of porosity. The edges of the specimens were protected with shellac. The tin was then gradually removed by anodic dissolution in 5 per cent. aqueous sulphuric acid. The process was stopped before the CuSn layer was exposed. The tin deposited on the cathode was removed and taken into solution and both that and the electrolyte were analysed jointly. Approximately 1 gm. of tin removed from a number of specimens gave a copper content of 0.39 per cent. Thus it is shown that when Chempur tin is employed, the coating contains an amount of copper agreeing with the microscopic evidence that the coating consists largely of eutectic, but containing regions of hypoeutectic composition; assuming the composition of the eutectic to be 0.94 per cent.¹

Discussion.

The phenomenon described above is one for which no explanation has yet been advanced, and the following mechanism is suggested as accounting for the formation of the striations.

The orientation of the etch-facets in a single crystal is normally controlled by the orientation of the crystal itself, and therefore cannot vary in one crystal. In the phenomenon under discussion, the orientation of the etch-facets does vary, and so cannot be entirely controlled by the crystal axes of tin crystals.

It is suggested that this peculiar etching habit of the tin coating is due to periodic changes of orientation of the CuSn crystallites in the eutectic colonies. Such a varying orientation is explained in the following manner.

The growth of any crystal from a melt takes place most rapidly in the direction in which the temperature gradient is greatest; if a large number

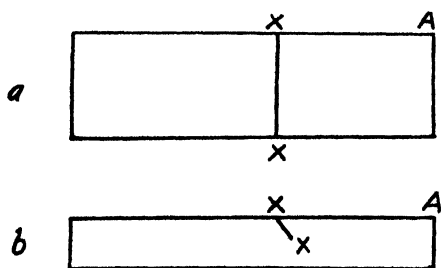


FIG. 7 (a) and (b).

of crystal nuclei are present, as in the solidification of the eutectic, those in which particular crystallographic directions, the directions of easy growth, coincide with the direction of greatest temperature gradient, will develop the fastest. Hence in the solidified eutectic there will be some relationship between the orientation of the CuSn compound with the direction

of the isothermals that exist when solidification takes place. The isothermals in a cooling body depend only upon the direction in which loss of heat occurs, and it is clear that with cooling conditions in a specimen of the type we are considering (Fig. 7a) that is cooling from the end A, loss of heat at any section XX is partly by conduction along the specimen towards A, and partly by conduction, convection and

¹ C. O. Hiers, G. P. de Forest, *Am. Inst. Min. Met. Eng. Inst. Met. Div.*, 1930, 207-218.

radiation from the surface at XX. The relation between these quantities will control the direction in the specimen of the isothermal plane that intersects the surface in XX. The isothermal plane will be inclined to the surface in a direction such as that indicated by XY in Fig. 7*b*.

Periodic variation in the direction XY will be set up by any periodic irregularity either in the loss of heat from the surface or in the flow of heat along the specimen. It is suggested that the latter is the fluctuating factor, and that the cause is alternate solidification of the eutectic under normal and supercooled conditions. Such alternations may be due to the loss of heat of the coating being too rapid to allow normal solidification to take place, except when the latent heat evolved by a supercooled portion in the act of freezing slows down the loss of heat by the next portion, permitting it to reach the true temperature of solidification.

Supercooling of the part of the surface immediately to the right of XX will cause more heat to flow from XX by conduction, making XY more nearly perpendicular to the surface. Solidification is accompanied by evolution of the latent heat, which will raise the temperature of the part concerned to the true freezing point, causing less heat to be conducted from XX to the right. While this is taking place, the isothermal XX is moving to the left, so if the process of superfusion alternates with normal freezing, the direction of XY will vary periodically between two limits. This will cause periodic variations in the orientation of the CuSn crystallites in the eutectic, which will in turn periodically vary the etch-facets formed in the tin surrounding the CuSn compound although the tin, being the continuous phase, persists in its unaltered orientation, and consists still of single crystals.

It must be realised that the foregoing theory is not limited to coatings of the eutectic composition only. In hyper-eutectic melts the primarily separated dendrites of the CuSn compound are disposed independently of the striations, their solidification having preceded the development of the eutectic. In coatings of the hypo-eutectic composition the primary separation of tin probably assists in delaying the solidification of the eutectic, and thus makes the visual appearance of the striations more pronounced.

The explanation suggested above, that the periodic release of latent heat when solidification takes place after supercooling controls the direction of heat flow and so the orientation of the CuSn crystallites in the eutectic, is not amenable to direct experimental verification, since the CuSn crystallites are too small to permit of any determination of their orientation. It appears, however, that the peculiar etching habit of the coatings must depend on the mode of solidification of the eutectic in some such manner as that suggested.

Summary.

Hot-dipped tin coatings on copper generally exhibit striations which are shown to occur within single crystals. Examination of a number of specimens by optical and metallographic methods shows the phenomenon to be related to the crystallisation of the Sn/CuSn eutectic.

The authors desire to make acknowledgment to the International Tin Research and Development Council for grants enabling the work to be prosecuted, to the Principal and Governors of the Sir John Cass Technical Institute for facilities, and to Mr. D. J. Macnaughtan, Director of Research, International Tin Research and Development Council, for his advice and interest.

THE BEHAVIOUR OF WATER HELD IN FINE-PORED MEDIA.

By B. H. WILSDON, D. R. G. BONNELL and Miss M. E. NOTTAGE.

Received 15th April, 1935.

The problem of the nature and magnitude of the force exerted between water and porous materials is a subject of considerable importance in many different fields of investigation. For example, the weathering of building materials may in some cases be greatly influenced by the retention of water within the fine pores; the availability of the soil water to plants, and the distribution of water in the soil, is of extreme importance to agricultural science; whilst, in the field of ceramics, problems of plasticity, shrinkage, etc., are bound up with those dealing with the adhesion of water to fine particles. The work now described was undertaken for the purpose of obtaining a better understanding of the forces to which the water held in porous building materials is subject. A primary consideration was to discover methods of examination which would be applicable at low water contents when the porous material might be described as no more than "damp."

Various experimental methods are available for measuring the attraction force between water and porous media, the chief of which are as follows:—

(1) *By the direct application of a hydrostatic tension to the moist porous system.* In this method a hydrostatic tension is applied and adjusted until it is in equilibrium with the tension exerted by the porous system. In this way a direct measure of the force exerted between water and the porous medium is obtained. The experiment may be carried out either statically or dynamically. A method has been described¹ by which a hydrostatic tension applied to a fine-pored reference material with which that to be investigated is placed in capillary contact may be used to determine the equilibrium pressures.

(2) *By balancing the tension within the system against a solution of known osmotic pressure, the porous system being separated from the solution by a semi-permeable membrane.*

(3) *By balancing the tension within the system against the known or calculated tension of a solution, equilibrium being reached through the vapour phase.* Since, according to generally accepted theories, the vapour pressure of a liquid is directly proportional to its hydrostatic pressure, it may be assumed that when the vapour pressures of the porous system and the solution are in equilibrium, their hydrostatic pressures are also equal, and the value for the latter may be calculated from the well-known formula:—

$$P = \frac{pw \log_{10} \frac{w}{w_1}}{S_0 \times 0.4343}$$

¹ *Report of the Building Research Board for the Year 1931*, p. 21.

where P = Pressure deficiency or tension within the porous system,
 p = Density of water at the temperature of the experiment.
 S_0 = Density of water vapour at the temperature of the experiment,
 w = Vapour pressure of water over a free water surface and
 w^1 = Vapour pressure of water within the porous medium.

(4) *By a determination of the freezing-point of water within the porous system, i.e., by observing the temperature at which the vapour pressure of the system is in equilibrium with that of ice.* The latter value can be ascertained from the published tables and the tension within the system calculated from the thermodynamical equation given above. It is to be noted that, in the osmotic, vapour pressure and freezing-point methods, pure water forms the mobile phase whilst in the hydrostatic tension method it consists of the liquid as a whole, which may be a solution if the test substance contains any soluble material. In the course of the present investigation all the above methods, with the exception of the freezing-point method, have been applied.

Experimental.

Two different types of materials were employed, *viz.* :—

(a) Materials of a colloidal nature which absorbed a high percentage of water, *e.g.*, clays such as ball-clay, kaolin and a burnt pozzolanic clay. These were thoroughly washed to remove all soluble salts.

(b) Materials which were granular in nature such as sands of various particle sizes and carborundum. The sands were freed from clay by washing with a dilute solution of sodium oxalate followed by thorough rinsing with distilled water. The carborundum was washed with benzene and then with distilled water.

All experiments were carried out at a thermostatically controlled temperature of 20° C.

Hydrostatic Tension (Dynamic) Method.

In this method a paste made of the material was packed around a porous pot which had been rendered impermeable to air either by precipitating a copper ferrocyanide membrane within the pores or by coating the outside with collodion. The pot was filled with water and connected to a mercury reservoir by means of which a hydrostatic tension could be applied to the water inside the pot and so to the water in the paste on the outside. The pot and material were completely enclosed—except for a fine capillary through which contact with the atmosphere was maintained—so that evaporation from the paste was eliminated.

For each material the desorption curve was determined, a slurry being used as the starting material and a small constant hydrostatic tension being applied until no more water was withdrawn from the system. The water content of the material was then determined and the hydrostatic tension readjusted at a slightly higher value. The absorption curves were determined in a similar manner by reducing the tension and so pushing water back into the system.

Hydrostatic Tension (Static Method).

A porous plate A (Fig. 1), coated with collodion and saturated with water, was sealed into a hollow brass holder C. The lower end of C was connected through tube B to a mercury reservoir by means of which a hydrostatic tension could be applied to the system. The space between the plate and the mercury was filled with air-free water. The moist paste

was placed on the upper side of A and contact between the water in the paste and that in B was made through the capillaries of A. To prevent

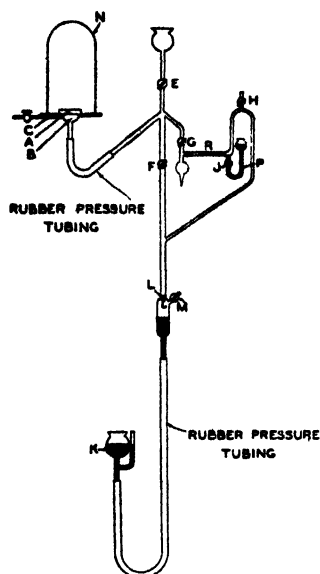


FIG. 1.—Apparatus for determining suction pressure.

pot according to the method recommended by Berkeley and Hartley.¹ The apparatus was then set up as shown in Fig. 2. The moist paste was packed around the pot which was filled with a sugar solution of known concentration. The passage of water into or out of the pot was indicated by the movement of the liquid in the capillary tube. The movement was observed through a microscope so that the amount of water extracted from the sugar solution or the clay was kept down to a minimum. The equilibrium pressure was found by bracketing, *i.e.*, the sugar solution was changed until two solutions were found whose concentrations were such that the osmotic pressure of the one was slightly greater and that of the other slightly less than that required to balance the pressure deficiency in the porous system. The water content of the paste was then determined and its freedom from sugar checked by testing with Fehling's solution.

Vapour Pressure Method.

A small quantity of the moist material was exposed to the vapour of a solution of known vapour pressure (potassium chloride solutions were used)

¹ Berkeley, Earl of, and Hartley, E. G. J. "The Osmotic Pressure of some Concentrated Aqueous Solutions." *Phil. Trans. Roy. Soc.*, 1906, 206A, 481.

² Szigeti, P. "Über sog. negative Adsorption und Dampfdruckisothermen an Permutiten und Tonen." *Koll. Beih.*, 1933, 38, 99.

³ Bouyoucos, G. "A Classification of Soil Moisture." *Soil Science*, 1921, 11, 33.

⁴ Parker, F. W. "Effect of Finely-divided Material on the Freezing-points of Water, Benzene and Nitro-benzene." *J. Amer. Chem. Soc.*, 1921, 43, 1011.

⁵ Thomas, M. D. "Aqueous Vapour Pressure of Soils." *Soil Science*, 1921, 11, 409.

⁶ Puri, A. N., Crowther, E. M. and Keen, B. A. "The Relation between the Vapour Pressure and Water Content of Soils." *J. Agric. Science*, 1925, 15, 68.

evaporation the paste and plate were enclosed by a vessel N. The hydrostatic tension was applied by adjusting the mercury level with taps F and G open. F was then closed, thus allowing the applied tension and that exerted by the clay to act on opposite ends of a mercury thread R contained in the horizontal capillary tube, the movement of which was observed with a travelling microscope. The taps marked E, H, and M were present to facilitate the removal of water and air from the apparatus. By repeated adjustment of the mercury level, the tension in equilibrium with that in the moist paste was obtained without alteration of the water content of the material.

The above two methods gave concordant results but their application is limited by the fact that under ordinary conditions of experiment it is not practicable to submit water to a tension greater than one atmosphere.

Osmotic Pressure Method.

A copper ferrocyanide membrane was precipitated within the pores of a porous

until equilibrium was reached. The hydrostatic tension within the paste was then calculated by means of the formula previously mentioned. Two forms of apparatus were used :—

(a) Four small glass bulbs (about 1 cm. in diameter) were sealed to the sides of a large oblong bulb which was fitted with a manometer and a removable stopper or bung. A small quantity of wet paste was injected into each of the small bulbs by means of a pipette and a solution of known vapour pressure was introduced into the large bulb so that the surface of the liquid was near to, but did not come into contact with, the wet paste. The apparatus was then evacuated, sealed up and left in a thermostat for several weeks. The bulbs were then cut off, quickly placed in weighing bottles and weighed. During this process the material was exposed to the atmosphere for not more than ten seconds. The water content of the pastes was then determined.

(b) Since the above apparatus lacked means for ascertaining the attainment of equilibrium a second form was devised with which a series of check results could be obtained. In this form a small quantity of wet paste on a light glass pan was fastened to the lower end of a silica spring suspended from the stopper of a tall glass jar. The lower part of the jar contained a solution of known vapour pressure, the surface of the solution being just below the wet paste. The apparatus was evacuated and kept in a thermostat. Variations in the length of the spring caused by variations in the water content of the paste were followed by observing with a microscope the distance between a marked point on the spring and a fixed independent point. When variations ceased to occur it was assumed that the vapour pressure of the porous system had become equal to that of the solution. The water content of the paste was then determined. By duplicating in this apparatus the strength of the solution and the material contained in one of the bulbs of the first form of apparatus, a check on the results given by the latter could be obtained.

The inherent difficulty of the vapour pressure method, especially at high relative humidities, lies in the fact that comparatively large differences in hydrostatic tension correspond to extremely small differences in vapour pressure. Special precautions were taken therefore :—

(a) To evacuate down to the vapour pressure of the system and to maintain this condition during the course of the experiment.

(b) To allow a considerable time to elapse for the attainment of equilibrium.

(c) To prevent temperature gradients within the apparatus as a result of which evaporation from, or condensation on, the paste might occur. To this end the apparatus was enclosed in a box fitted with an electrically driven fan and the whole placed in a thermostatically controlled chamber.

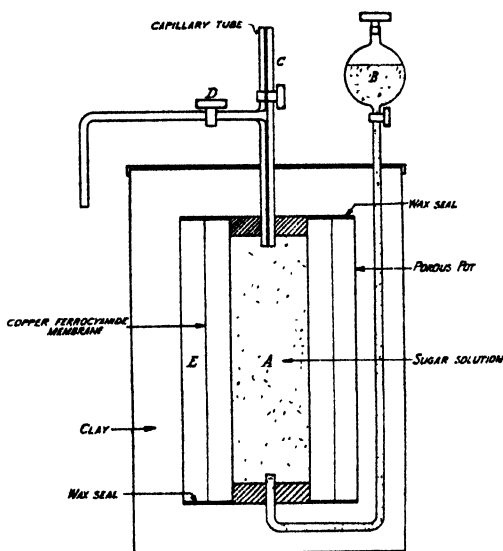


FIG. 2.—Apparatus for measuring pressure deficiency by an osmotic method.

Results.

In the table the equilibrium pressures observed by the hydrostatic and osmotic methods respectively are recorded. The moisture contents are expressed on a dry basis, *i.e.*, number of grams of water to 100 grams of material dried at 110° C. :—

Water Content.	Pressure (Atmos.).		Water Content.	Pressure (Atmos.).	
	Hydrostatic Tension Method.	Osmotic Pressure Method.		Hydrostatic Tension Method.	Osmotic Pressure Method.
Kaolin.			Pozzolana.		
66.8	—	.50	60.8	—	0.95
66.8	—	.63	59.1	—	1.63
66.3	—	1.00	55.6	0.048	—
66.0	—	1.43	49.0	—	4.43
65.3	—	1.60	48.0	0.160	—
63.1	0.063	—	42.7	0.234	—
59.2	—	2.87	42.5	—	5.41
45.5	0.224	—	37.7	0.378	—
40.7	0.316	—	36.5	0.394	—
39.1	0.369	—	35.8	0.468	—
38.2	—	28.15	35.4	—	9.26
36.86	0.453	—	35.2	—	9.58
35.8	0.645	—	34.8	—	7.69
35.6	0.528	—	33.7	0.546	—
35.3	0.645	—	33.1	0.666	—
35.1	—	34.7	32.6	0.715	—
26.7	—	49.4	32.4	0.742	—
20.3	—	68.7	32.9	0.878	—
16.6	—	126.8	28.5	—	16.5
7.35	—	173.7	22.0	—	37.2
6.59	—	193.9	20.6	—	53.1
			16.1	—	100.8
			6.7	—	162.5
Ball Clay.			Carborundum.		
180.3	—	0.37	35.3	0.108	—
162.1	—	0.78	33.2	—	0.86
92.3	0.041	—	32.9	0.301	—
67.3†	—	1.8†	32.8	—	1.05
66.2	—	1.64	29.7	0.590	—
56.8	0.105	—	29.6	—	3.14
47.5	—	3.31	23.9*	—	4.6*
47.1	0.238	—			
40.2	0.397	—			
39.5†	—	3.6†			
37.7	0.375	—			
29.9	0.849	—			
29.7	—	16.4			
25.9*	—	16.0*			
22.1*	—	54.5*			
20.2	—	52.7			
15.5	—	104.0			
5.6†	—	139.0†			
			Sand.		
			23.09	—	0.85
			23.09	—	0.88
			12.0	—	3.8
			8.43*	—	4.6*
			7.78	0.066	—
			0.68	0.234	—

* Result obtained by the vapour pressure method (a).

† Result obtained by the vapour pressure method (b).

Discussion.

The outstanding feature of these results is the wholly unexpected discrepancy between the values obtained by the hydrostatic tension method on the one hand and the osmotic and vapour pressure methods

on the other, the latter being several times greater than the former for the same water content of the porous material. A careful search for possible sources of experimental error was of no avail. The non-specific effect of the membrane was proved by using both types of membrane (*vis.* copper ferrocyanide and collodion) for the hydrostatic tension (suction) experiments; the pressure-water content curves so obtained were coincident. In one experiment the apparatus was arranged in such a way that the same porous pot, membrane and sample of clay served for both hydrostatic and osmotic pressure measurements. The results obtained were:—

Water content of clay (kaolin) (dry basis) = 36.2 per cent.

Hydrostatic tension = 40.95 cms. Hg = 0.538 atmos.

Osmotic pressure = 28.15 „

The materials were all well washed and analyses showed that they contained no soluble salts whereby an equilibrium of the Donnan type could have been set up. Parenthetically, it may be noted that such an equilibrium would have affected the results in the opposite sense, *i.e.*, a decreased value for the observed osmotic pressure would have been obtained. The point was, however, tested experimentally by a determination of the osmotic pressure of kaolin sedimented from a 5 per cent sodium chloride solution. The results obtained were:—

Water content of the clay (dry basis) = 38.7 per cent.

Percentage of sodium chloride in the dry clay = 0.198 „

Hydrostatic tension (static method) = 15 cms. Hg = 0.197 atmos.

Osmotic pressure = 1.99 „

It is important to note that the salt concentration, which must be assumed to exist in the liquid removed by a hydrostatic tension in order that the difference in the work done hydrostatically and osmotically shall account for the observed differences in the pressures, is far higher than is possible.

A critical survey of the literature showed similar anomalies when the experimental data obtained by other workers were calculated to a common basis. In Fig. 3 are reproduced some pressure/moisture-content curves calculated from such data together with data obtained during this investigation for kaolin and sand. The curves show clearly that the values obtained by the direct application of a hydrostatic tension (method 1) are of a different order of magnitude. It is interesting to note that anomalous results have also been obtained in the study of other properties of porous systems.

Shereshefsky⁸ found that the lowering of the vapour pressure in small capillaries (5.3μ radius or less) is greater than that calculated from the Kelvin equation, and he suggested that the classical theory as applied to vapour pressure lowering in small capillaries is incorrect.

Glaxelli and Wiertelak⁹ obtained values for the electro-kinetic potential of silica gels which were 10-100 times smaller than those usually obtained. After ignition of the gel, however, the values became normal. They attributed the anomalous results obtained with the unignited gel to the presence of fine pores in which, the water is, to some extent,

⁸ Shereshefsky, J. L. "Vapour Pressure in Small Capillaries." *J. Amer. Chem. Soc.*, 1928, 50, 2966.

⁹ Glaxelli, S. and Wiertelak, J. "Das Elektrokinetische Potential des Kiesel-saure Gels." *Koll. Z.*, 1927, 43, 85.

bound by the gel and is therefore less free to move under the applied electro-motive force.

White, Urban and van Atta¹⁰ have shown that stream potentials measured in pyrex glass capillaries less than $5\ \mu$ in diameter decrease to a value which is 0.25 per cent. of that obtained with larger capillaries.

Wolkowa¹¹ in his measurements of the velocity of penetration of liquids into powdered materials such as silica gel, kaolin, and clays found that the mean radius of the pores calculated from data obtained with non-polar liquids was constant but that the value calculated when

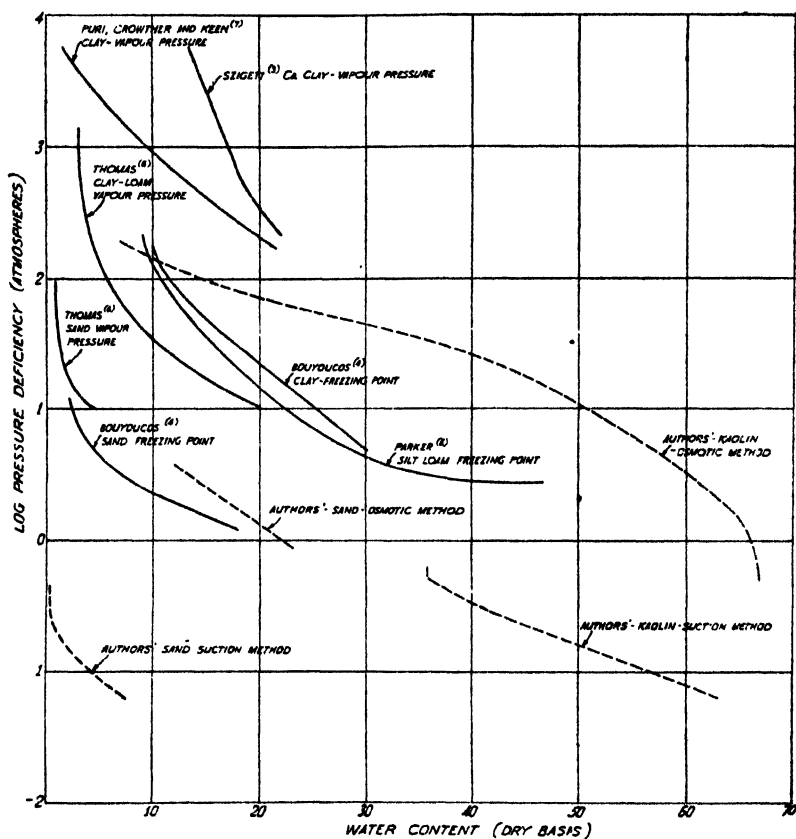


FIG. 3.

polar liquids were used was smaller and variable and he suggested the formation of oriented films on the surface of the particles as a possible explanation of this result.

Smith-Rose¹² found that the conductivity of the soil tends to increase with tightness of packing up to moisture contents of 20 per cent. and

¹⁰ White, H. L., Urban, F. and Van Atta, E. A. "Correlation of Stream Potentials and Surface Conductance." *J. Phys. Chem.*, 1932, **36**, 3152.

¹¹ Wolkowa, Z. W. "Porositätsbestimmungen von Dispersoiden nach der Eindringgeschwindigkeit von Flüssigkeiten." *Koll. Z.*, 1934, **67**, 280.

¹² Smith-Rose, R. L. "Electrical Properties of Soil." *Proc. Roy. Soc.*, 1933, **140A**, 359.

more. The value of the dielectric constant and its variation with frequency are also anomalous; at low radio frequencies he obtained values for the dielectric constant which were greater than the value obtained with pure water.

These facts all seem to point to the general conclusion that the conditions postulated in the deduction of formulæ applicable to coarse systems are, in some way, unfulfilled in fine-pored systems. In all the formulæ used for the calculation of data obtained by the experimental methods described above, it is assumed that the molecules of the liquid in the pores of the material are in exactly the same state as they are in a large bulk of the liquid. The lower limit of thickness of a film beyond which the liquid exists under the influence of surface forces is at present an open question. McHaffie and Lenher¹³ have obtained films of water up to 5.3×10^{-6} cms. thick on plane surfaces of glass by adsorption from the vapour phase; up to this thickness the vapour pressure of the water in these films is less than the saturation pressure at the same temperature.

As a means of reconciling the anomalous results obtained by us and by other workers, we suggest that Hardy's¹⁴ conception of molecular orientation in thin liquid films on solid surfaces may be applicable to the thin films of water contained in fine-pored systems. This conception may be briefly stated thus:—

The direct influence of the molecular forces of attraction exerted by a solid at an interface is confined mainly to a monomolecular adsorbed layer. The action of this attraction field is, however, directive, and may produce a polarisation of the adsorbed molecules which is transmitted to superincumbent layers. In this way a solid surface causes the molecules of a liquid in its proximity to become arranged in an orderly manner in layers parallel to the surface, the orderly arrangement decreasing as the distance from the surface increases. The planes separating the layers are equipotential surfaces and form natural cleavage planes, the work required to make the layers slip over one another being small compared with the work required to remove the molecules beyond the range of the orienting forces.

In fact the film in the direction at right angles to the surface may perhaps be considered to behave as though it were a crystalline material while in directions parallel with the surface it behaves as a liquid. The vapour pressure of the film may then be regarded as possessing different values in the two directions. The vapour pressure at the free surface would correspond with that of a solid while the two-dimensional vapour-pressure along the surface would determine the work done in removing water from the film by a hydrostatic tension and no simple relation would relate it with the work necessary to pluck out a molecule from the surface "by the roots."

The relation between hydrostatic tension on the one hand and osmotic and vapour pressure on the other, will only become normal when the molecules of water lie beyond the range of the orienting forces, *i.e.*, when they exist in the same state as they do under a free water surface.

It is recognised that the data supplied in this paper are hardly sufficient to justify an attempt at a more detailed treatment of the factors

¹³ McHaffie, I. R. and Lenher, S. "The Adsorption of Water from the Gas Phase on Plane Surfaces of Glass and Platinum." *J.C.S.*, 1925, 127, 1559.

¹⁴ Hardy, Sir W. B. "Problems of the Boundary State." *Phil. Trans.*, 1932, 230A, 1.

which give rise to the "anomalous" results discussed, but it is hoped that further work on this interesting problem may supply the necessary information.

Summary.

The methods applicable for the investigation of the behaviour of water in fine-pored systems are discussed.

It is shown that methods depending on the application of Kelvin's equation for the lowering of vapour pressure in capillaries do not lead to the same results as are obtained by the methods in which a hydrostatic tension is employed.

The cause of these anomalous results together with a possible explanation is discussed.

THE TERNARY SYSTEM POTASSIUM FLUOBORATE—POTASSIUM PERIODATE—WATER AT 85°.

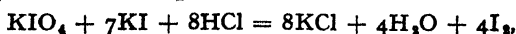
BY R. C. RAY AND H. C. MITRA.

Received 3rd June, 1935.

It has been shown previously that with potassium fluoborate, potassium permanganate yields a stable double salt,¹ and potassium perchlorate forms two double salts,² both of which are readily decomposed by water. It was, therefore, proposed to make a phase rule study of the ternary system described in this paper in order to find out the behaviour of potassium periodate which is the only other known compound of the same type. The composition of the solid phase was determined, as before, by Schreinemaker's residue method.³

Pure samples of potassium fluoborate and potassium periodate were obtained by recrystallisation. The potassium periodate was proved to be free from iodate, and the purity of the two salts were tested by estimation of potassium and iodine content respectively. Mixtures of the two salts and water were made in various proportions in the usual manner, and they were stirred mechanically in a thermostat at $35^\circ \pm 0.1^\circ$. Equilibrium was obtained in three days, and this was proved in many cases by keeping the mixtures for longer periods and making a second and sometimes a third analysis.

When equilibrium was established, the solid was rapidly separated from the liquid phase, and the composition of both the solution and the "wet solid" was determined. The same procedure was followed for the analysis of the solid as well as of the solution. The amount of potassium periodate was estimated by adding an excess of potassium iodide solution to the solution of a mixture of the two salts acidified with hydrochloric acid. The following reaction takes place:



so that one-eighth of the liberated iodine is that due to potassium periodate. The method has been described by Malaprade,⁴ and given in Scott.⁵

¹ Ray and Chatterji, *Journ. Chem. Soc.*, 1932, p. 384.

² Ray and Mitra, *Trans. Faraday Soc.*, 1934, **30**, 1161.

³ *Z. physikal. Chem.*, 1893, **11**, 81.

⁴ *Bull. Soc. chim.*, 1926, **39**, 330.

⁵ *Standard Methods of Chemical Analysis*, 1926, **1**, 224.

Kimmins⁶ also used the same method previously, but he heated the mixture of the periodate, the iodide solution and hydrochloric or sulphuric acid in a stoppered bottle for six hours in boiling water. Partington and Bahl⁷ have recently shown that the reaction is not quite complete in the cold, and then a slightly low value is obtained for iodine, but the method gives a fairly accurate result if the reaction mixture is heated for about fifteen minutes at 60°. The amount of potassium fluoborate was obtained from the estimation of the total potassium.

The results of analysis of the solutions and their corresponding wet solids are plotted in a triangular diagram, the relevant corner of which is shown in the accompanying figure. It will be noted that the curve

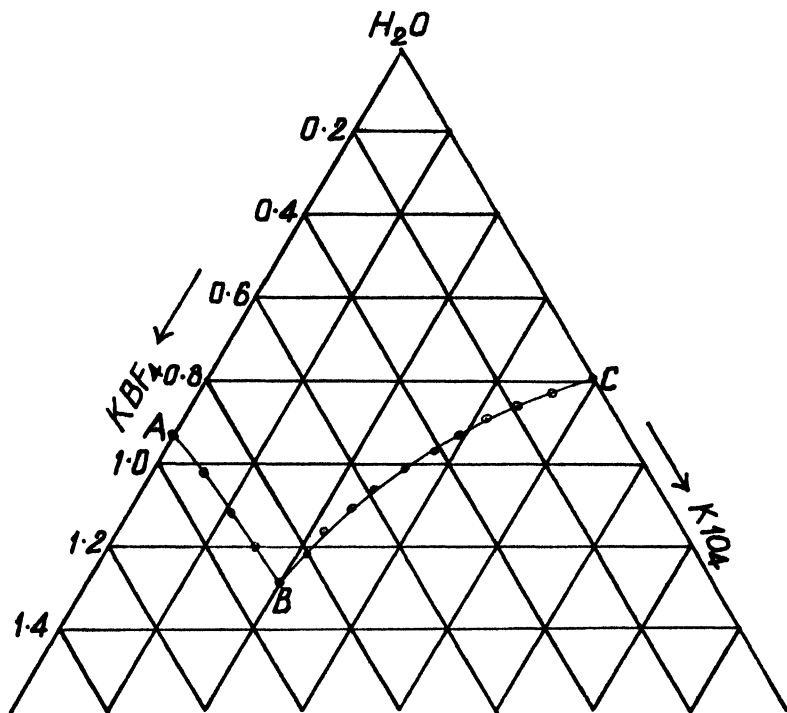


FIG. 1.

consists of only two portions, AB and BC, representing the saturation curves of potassium borofluorate and potassium periodate respectively, and there is no indication of the formation of any double salt.

In the case of a series of chemical compounds of the same type, it seems reasonable to suppose that a double salt would easily form between any two of them if their ionic domains were of the same size and shape. It appears likely that when the size of the radical, as in the case of IO_4^- , is too large, it cannot replace the BF_4^- in the crystal lattice of potassium fluoborate and no double salt formation can take place, but when the size of the radical, such as MnO_4^- , is sufficiently small, a stable double salt is readily formed.

⁶ *Jour. Chem. Soc.*, 1887, 51, 356.

⁷ *Ibid.*, 1934, p. 1087.

Summary.

The system $\text{KBF}_4\text{--KIO}_4\text{--H}_2\text{O}$ has been studied at 35° . No indication of the formation of any double salt has been found. It is suggested that as the size of the IO_4^- is probably larger than the BF_4^- , the former cannot take the place of the latter in crystal lattice of potassium fluoborate, while MnO_4^- being smaller in size can easily do so. Thus no double salt formation occurs in the first, but a stable double salt is formed in the second case.

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THE SCATTERING OF LIGHT IN PROTEIN SOLUTIONS.

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It is not possible to decide from what is known as to the scattering of light in protein solutions whether the intensity of the scattered light and the molecular weight of the protein are simply related. Other factors, such as the p_H value, seem to be as important as the particle dimensions themselves. These intricacies may well arise from a bad choice of the experimental materials or from inadequate experimental conditions. As an example we may take the careful measurements of Holwerda¹ on casein sols, who showed that in 0.1 per cent. casein sols containing 9 milliequivalents NaCl per litre, the intensity of the scattered light stands in the ratios 389 : 224 : 116 when the p_H of the solutions reaches the values 7.4, 8.1 and 10.2 respectively. However, it has been shown by Svedberg, Carpenter and Carpenter^{2, 3} that casein is poly-disperse and that it is impossible to use dilute alkali as a solvent without irreversibly disrupting the protein molecule. Holwerda's solutions were prepared by stirring the casein for about 18 hours with water and NaOH at about 7°C ., which suffices to explain the decrease in light scattering when more alkali is added to reach the higher p_H values. It is, therefore, difficult to interpret correctly the increase due to small amounts of NaCl in these decomposed systems.

To obtain satisfactory results it is essential to start with solutions containing uniform particles of known dimensions. Owing to the work of Svedberg⁴ we actually know a large number of proteins which satisfy these requirements.

For the present investigation we have chosen : ovalbumin, amandin, excelsin and haemocyanin (of *Helix Pomatia*). Their molecular weights

¹ B. J. Holwerda, *Rec. trav. chim.*, 1931, 50, 601.

² T. Svedberg, L. M. Carpenter and D. C. Carpenter, *J. Am. Chem. Soc.*, 1930, 52, 241-701.

³ D. C. Carpenter, *J. Am. Chem. Soc.*, 1935, 57, 129.

⁴ T. Svedberg, *Kolloid Z.*, 1930, 51, 10; *Trans. Faraday Soc.*, 1930, 26, 740; *Chem. Rev.*, 1934, 14, 1; *Naturwiss.*, 1934, 22, 225; *Science*, 1934, 79, 327; *Ber.*, 1934, 67, 117.

as determined by the ultracentrifuge are: 34,500 for ovalbumin,^{5, 6, 7} 208,000 for amandin,⁸ 212,000 for excelsin⁸ and 5,000,000 for haemocyanin.⁹

It is our purpose to establish the ratio of the light scattered by these proteins relatively to each other. Under certain conditions, which we shall make clear, that ratio is proportional to the ratio of their molecular weights.

We take as a basis of our considerations, the equation of Rayleigh,^{10, 11} which may be written in the following form

$$\frac{i_0}{I} = \frac{9\pi^2}{2\lambda^4 N} \left[\frac{n_2^2 - n_1^2}{n_2^2 + 2n_1^2} \right]^2 \frac{6(1 + \rho)}{6 - 7\rho} \phi^2 g.M. \quad (1)$$

The scattering power i_0/I is defined as the ratio of: i_0 (the intensity of the light scattered by a unit of volume, measured at unit distance and at 90° to the path of the incident light), to I (the intensity of the beam of unpolarised incident light.) The scattering power is thus a function not only of the molecular weight of the protein, but of several other factors which we will consider briefly.

The partial specific volume ϕ of the protein in solution is practically the same for all proteins, and independent of the composition of the solution. The values of ϕ are taken from the papers of Svedberg and are mentioned in the table of results.

The values of the refractive indices of the protein n_2 and the solvent n_1 are calculated (on the assumption that the refractive index of the solution n is an additive property) from the equation

$$n = g\phi n_2 + (1 - g\phi)n_1.$$

The value of n_2 for ovalbumin used is based on the experiments of Haas¹²; that for excelsin on the values of Schmidt¹³ for edestin: these two proteins being very alike as to their amino-acid composition, which is the determining factor in the refractivity of a protein. The value of n_2 for amandin is based on a few personal determinations and must be considered as provisional. The index for haemocyanin is an average of the refractive indices, found for a series of haemocyanins of different species, based on the data assembled by Redfield.¹⁴

The table of results gives the values of the refractive index of the solutions, n , for sodium light, and the calculated value of $\left[\frac{n_2^2 - n_1^2}{n_2^2 + 2n_1^2} \right]^2$ under the name of refractive index factor.

The depolarisation ρ has been determined by photographic photometry by the method of Cornu as described by Cabannes.¹⁵ The Cabannes factor $\frac{6(1 + \rho)}{6 - 7\rho}$ is given in the table of results for each solution. As

⁵ T. Svedberg and J. B. Nichols, *J. Amer. Chem. Soc.*, 1926, **48**, 3081.

⁶ J. B. Nichols, *J. Am. Chem. Soc.*, 1930, **52**, 5176.

⁷ B. Sjögren and T. Svedberg, *J. Amer. Chem. Soc.*, 1930, **52**, 5187.

⁸ T. Svedberg and B. Sjögren, *J. Amer. Chem. Soc.*, 1930, **52**, 279.

⁹ T. Svedberg and E. Chirnoaga, *J. Amer. Chem. Soc.*, 1928, **50**, 1399.

¹⁰ J. W. Strutt, *Phil. Mag.*, 1871, **41**, 107 and 477; *ibid.*, 1899, **47**, 375.

¹¹ W. S. Stiles, *Phil. Mag.*, 1929, **7**, 204.

¹² A. R. C. Haas, *J. Biol. Chem.*, 1918, **35**, 119.

¹³ C. L. A. Schmidt, *J. Biol. Chem.*, 1915, **23**, 487.

¹⁴ A. C. Redfield, *Biological Rev.*, 1934, **9**, 189.

¹⁵ J. Cabannes, *La diffusion moléculaire de la lumière*. Presses Universitaires, Paris, 1929.

Preparation No.	Concentration Grs. Protein/c.c.	Refractive Index of Solution.	Refractive Index Factor.	Caban- nes Factor.	$\lambda = 5769 \text{ and } 5790.$			
					Relative Scattering Power.	Correction Factor for Absorption.	Specific Relative Scattering Power.	$K \times M \times 10^{-8}$.
Ovalbumin : $p_H = 4.60$ $\phi = 0.748$ $n_2 = 1.5686$								
F 10	0.0202	1.3380	0.0127	1.008	0.239	1.025	12.10	1.68
G 6	0.0206	1.3400	0.0125	1.008	0.223	1.015	10.98	1.56
F 4	0.0234	1.3406	0.0125	1.008	0.274	1.027	12.01	1.71
G 5	0.0311	1.3440	0.0122	1.010	0.272	1.015	8.88	1.28
G 3	0.0370	1.3463	0.0121	1.010	0.308	1.013	8.43	1.23
G 4	0.0412	1.3480	0.0120	1.011	0.402	1.023	9.98	1.47
F 3	0.0518	1.3493	0.0121	1.012	0.480	1.024	9.48	1.39
G 2	0.0617	1.3557	0.0115	1.013	0.467	1.028	7.77	1.20
F 9	0.0808	1.3572	0.0117	1.015	0.633	1.052	8.23	1.23
F 1	0.1031	1.3650	0.0113	1.017	0.771	1.030	7.70	1.20
F 2	0.1036	1.3663	0.0111	1.017	0.787	1.045	7.93	1.25
F 8	0.1617	1.3793	0.0108	1.027	1.135	1.097	7.69	1.24
Armandin : $p_H = 5.54$ $\phi = 0.748$ $n_2 = 1.589$								
A 3	0.0054	1.3445	0.0138	1.009	0.403	1.027	76.52	9.84
A 2	0.0108	1.3436	0.0139	1.010	0.747	1.123	77.60	9.91
B 5	0.0185	1.3491	0.0137	1.011	1.080	1.155	69.74	8.97
B 4	0.0371	1.3514	0.0138	1.014	1.803	1.289	62.66	8.00
B 1	0.0732	1.3562	0.0139	1.021	2.430	1.613	54.60	6.87
B 3	0.0742	1.3559	0.0140	1.021	2.354	1.623	51.32	6.41
Excelsin : $p_H = 6.9$ $\phi = 0.748$ $n_2 = 1.5686$								
A 3	0.0092	1.3500	0.0111	1.009	0.525	1.151	67.11	10.72
A 8	0.0122	1.3511	0.0110	1.010	0.644	1.211	62.68	10.10
B 3	0.0156	1.3520	0.0110	1.011	0.784	1.259	61.40	9.90
A 7	0.0214	1.3515	0.0112	1.012	0.938	1.393	62.59	9.90
A 1	0.0306	1.3501	0.0115	1.013	1.153	1.611	61.86	9.55
B 2	0.0312	1.3571	0.0107	1.013	1.151	1.612	59.01	9.77
B 1	0.0416	1.3612	0.0105	1.015	1.284	1.892	56.47	9.54
A 5	0.0456	1.3582	0.0109	1.016	1.179	2.052	52.74	8.51
A 4	0.0612	1.3672	0.0102	1.019	1.127	2.541	47.15	8.12
Haemocyanin : $p_H = 5.85$ $\phi = 0.735$ $n_2 = 1.6008$								
D 5	0.000128	1.3320	0.0166	1.006	0.298	1.032	2391	265.
D 4	0.000128	1.3322	0.0166	1.006	0.293	1.054	2404	266.
D 6	0.000321	1.3321	0.0166	1.007	0.702	1.100	2395	265.
D 2	0.000321	1.3322	0.0166	1.007	0.674	1.028	2157	239.
E 1	0.000356	1.3321	0.0166	1.007	0.803	1.144	2583	286.
D 7	0.000642	1.3320	0.0167	1.008	1.260	1.259	2467	272.
D 1	0.000642	1.3325	0.0165	1.008	1.245	1.262	2444	273.
D 8	0.001285	1.3326	0.0165	1.009	2.060	1.646	2620	292.
D 3	0.001285	1.3329	0.0165	1.009	2.020	1.622	2579	288.

will be apparent from an inspection of that table, the depolarisation plays a negligible rôle in the light-scattering of the proteins here studied. This is, however, due to the fact that we have purposely chosen proteins with very low depolarisation (so-called "isotropic" proteins); for other proteins the depolarisation may become very significant.

Although generally important, the factors so far considered are secondary and it is evident that the extent to which the results can be depended upon rests on the accuracy with which the scattering power can be determined. The conditions to be realised to this end will now be explained.

$\lambda = 5461.$				Total Light Hg. Arc.			
Relative Scattering Power.	Correction Factor for Absorption.	Specific Relative Scattering Power.	$K \times M \times 10^{-3}$.	Relative Scattering Power.	Correction Factor for Absorption.	Specific Relative Scattering Power.	$K \times M \times 10^{-3}$.
0.211	1.010	10.55	1.47	0.192	1.013	9.61	1.55
0.201	1.013	9.88	1.40	0.175	1.018	8.65	1.39
0.250	1.023	10.80	1.53	0.230	1.025	10.07	1.62
0.247	1.022	8.11	1.17	0.227	1.038	7.61	1.22
0.275	1.036	7.69	1.12	0.264	1.024	7.28	1.17
0.378	1.032	9.47	1.40	0.328	1.044	8.31	1.34
0.441	1.034	8.80	1.29	0.397	1.040	7.82	1.26
0.428	1.041	7.21	1.11	0.392	1.059	6.70	1.08
0.575	1.064	7.55	1.13	0.507	1.066	6.68	1.07
0.695	1.062	7.15	1.11	0.627	1.059	6.43	1.03
0.711	1.068	7.33	1.15	0.614	1.080	6.40	1.03
1.027	1.120	7.10	1.14	0.892	1.129	6.21	1.00
0.371	1.034	71.35	9.18	0.335	1.045	64.72	8.32
0.678	1.099	68.92	8.80	0.575	1.138	63.59	8.12
1.004	1.190	64.46	8.29	0.909	1.229	60.23	7.75
1.610	1.365	59.23	7.56	1.355	1.370	48.32	6.17
2.069	1.755	49.49	6.23	1.662	1.795	40.53	5.10
1.973	1.765	46.91	5.86	1.592	1.800	38.61	4.82
0.470	1.175	62.10	9.92	0.404	1.186	53.87	8.60
0.577	1.242	58.95	9.51	0.492	1.259	50.99	8.22
0.689	1.313	54.93	8.85	0.600	1.334	48.54	7.82
0.823	1.452	57.02	9.02	0.674	1.490	48.62	7.69
0.999	1.706	59.64	9.20	0.790	1.771	47.38	7.31
1.009	1.726	56.53	9.36	0.802	1.779	45.09	7.47
1.070	2.061	51.12	8.63	0.850	2.163	41.45	7.00
0.981	2.224	48.60	7.83	0.754	2.339	38.82	6.26
0.915	2.911	43.26	7.44	0.717	3.112	34.13	5.87
0.267	1.029	2143	237.	0.242	1.031	1976	219.
0.266	1.039	2148	238.	0.242	1.034	2003	222.
0.634	1.111	2191	243.	0.558	1.130	1958	217.
0.611	1.191	2265	251.	0.561	1.100	1922	213.
0.734	1.153	2380	264.	0.638	1.136	2034	225.
1.159	1.284	2315	255.	0.997	1.304	2022	223.
1.134	1.289	2275	254.	0.989	1.304	2008	224.
1.848	1.676	2415	269.	1.548	1.746	2104	235.
1.817	1.676	2368	264.	1.537	1.721	2065	230.

Preparation of the Proteins.

At first sight it would seem sufficient to use those methods of preparation which were found by the ultracentrifugal technique to give homogeneous products. This is not true, however, because the light scattering is particularly sensitive to the presence of even minute amounts of substances having very large particle dimensions; such impurities will be thrown to the bottom of the ultra-centrifuge cell during the first moments of centrifuging and will probably not cause any harm. Edestin may be taken as an instance. Even the best of our preparations could

not be freed from a small amount of very high-mass particles, whose presence in the ultracentrifuge preparations is also evident from the diagrams on page 187 of the publication by Lamm.¹⁶ To track these dangerous admixtures we have whenever possible examined separately the head and tail fractions obtained by fractional precipitation. This is a useful but not a decisive test, because—as is the case with Edestin—it may be impossible to separate the impurity by precipitation when its concentration has fallen below a certain limit.

In the case of proteins extracted from oleaginous seeds, extraction with organic solvents has been used to eliminate the oils and fats, traces of which cause turbidity and large errors.

1. Ovalbumin.

Ovalbumin was prepared by the Sørensen procedure¹⁷ except that the slow filtrations were replaced by centrifuging. Three recrystallisations only were made; no dialysis was used; the solutions to be examined were prepared by dissolving the mass of crystals in the required amount of water. These solutions were henceforth in the neighbourhood of the iso-electric point and contained a somewhat large concentration of ammonium sulphate. We were forced to operate in this way because it was observed that concordant results were only obtained with very rapidly prepared ovalbumin, maintained at low temperatures, and examined immediately after being put in solution. Dialysed solutions, old preparations, or preparations obtained from imperfectly fresh eggs gave quite erratic results. The determination of the concentration of the protein was done by heat coagulation according to M. and S. P. L. Sørensen¹⁸ and nitrogen determination in the coagulum (protein = $6.45 \times N$).

2. Amandin.

The almonds were extracted with 10 per cent. NaCl; the solution was precipitated by an equal volume of saturated ammonium sulphate, the precipitate redissolved in a phosphate buffer at p_H 5.6 containing 1 per cent. NaCl and the solution centrifuged to separate the fats. The still milky solution was finally completely freed from grease by treating it at $-23^\circ C$. with a mixture of alcohol and ether according to Hewitt¹⁹ and extracting the precipitated mass by alcohol-free ether in a Soxhlet apparatus. After elimination of the ether the powder was dissolved in the phosphate-NaCl mixture already described. After filtration a perfectly clear solution was obtained; the amandin was again precipitated by ammonium sulphate, redissolved and dialysed in the ice chest at $+3^\circ$, against the phosphate NaCl solution. After 3 to 4 weeks dialysis, the ammonium salts were eliminated; a precipitate had formed in the collodion bag; this precipitate redissolved in the buffer-mixture was the B sample, the mother solution the A sample.

The amandin concentration was determined by a nitrogen determination directly on the solution (protein = $5.26 \times N$).

3. Excelsin.

The endosperm of Brazil nuts was extracted in a Soxhlet apparatus with alcohol free ether; after aeration of the powder to eliminate the ether, it was treated with a 3 per cent. ammonium sulphate solution. To the filtered solution, saturated ammonium sulphate was added up to incipient precipitation; the precipitate was filtered off and discarded;

¹⁶ O. Lamm, *Z. physikal. Chem.*, 1928, 138, 313.

¹⁷ S. P. L. Sørensen and M. Høyrup, *Compt. rend. Carlsberg*, 1915, 12, 12.

¹⁸ M. and S. P. L. Sørensen, *ibid.*, 1925, 15, No. 9.

¹⁹ L. F. Hewitt, *Biochem.*, 1927, 21, 216.

the remaining solution was then precipitated by adding ammonium sulphate solution to bring the system to 60 per cent. of saturation. The precipitate thus obtained was treated a second time in the same way: this was done to eliminate the last traces of fatty material.

The perfectly clear solution was now fractionally precipitated by adding ammonium sulphate solution to obtain a first precipitate (sample A) and, after centrifuging, continuing the precipitation in the solution to obtain a second precipitate (sample B). Just as in the case of amandin, it appeared possible in this way to detect eventually the non-homogeneity of the preparation. The results show that this was not the case.

It is quite difficult to maintain the excelsin in solution at low temperature and the precipitates formed during dialysis could not be redissolved again. Fearing degradation, we avoided dialysis or ageing of the solutions by dissolving the precipitates in 10 per cent. NaCl just before beginning the measurements. The concentration was determined by precipitating the protein with an equal volume of trichloroacetic acid at 20 per cent., washing the precipitate with a 10 per cent. solution of this acid, and determining the N content of the precipitate (protein = $5.49 \times N$).

4. Haemocyanin.

After collection of the blood of 500 snails (*Helix Pomatia*) by heart puncture (total volume approx. 1200 c.c.) and centrifuging, the haemocyanin was precipitated by adding an equal volume of ammonium sulphate saturated solution; the precipitate was redissolved in 5 per cent. ammonium sulphate, the solution filtered and the operation repeated three times. The solution was then dialysed at $+3^{\circ}$ for twenty days: a crystalline precipitate formed, constituting sample E, the mother solution being labelled sample D. From the concentrated solutions, whose concentration was determined by the Kjeldahl method (protein = $6.49 \times N$) the other solutions were prepared by diluting with a phosphate buffer mixture (equal parts) (0.03 M). This preparation of haemocyanin was similar to that used by Redfield, Coolidge and Shotts²⁰ for *Limulus* haemocyanin.

Preparation of the Solutions.

The solutions prepared with the purified proteins are not fit for immediate measurement because they contain a variable amount of suspended material formed of dust particles and filaments of degraded protein. To eliminate these we have used for some time the "enveloping" method by means of aluminium hydroxide or aluminium phosphate; beautiful solutions are thus obtained, but they give results far more at variance than the untreated solutions. As found afterwards this is due to the incomplete elimination of the Al compounds. We abandoned this practice as it was found possible to eliminate the suspended particles by strong centrifuging (4000 r.p.m. at least) in a closed lute and careful transference to the cross-tubes by means of a syphon. If the cross-tube and syphon are first cleaned with chromic-sulphuric acid mixture and, after copious washing, dried at a somewhat high temperature (130-140°) and then they are cooled and handled in the way customary to microbiologists, as if to keep the apparatus aseptic, it is found that suspended material has been reduced to a negligible amount. The cross-tubes (see later) are made in such a way as to allow this very thorough cleaning and intensive drying.

It is necessary to ascertain that the operation has been successful: this may be easily done by placing the cross-tube in the measuring apparatus and looking at it through a magnifying glass put in the place of the photo-electric cell (see later). The solutions are never completely free from reflecting particles: these continue to decrease in number on leaving the

²⁰ A. C. Redfield, Th. Coolidge, and M. A. Shotts, *J. Biol. Chem.*, 1928, **76**, 188.

cross-tube undisturbed for an hour or so in the thermostat, up to a point where careful search reveals only two or three particles. The error thus introduced must be negligibly small, because distilled water which had been redistilled and protected from dust, and which showed many brilliant points when examined as described, did not perceptibly influence the photoelectric cell. This shows, too, that a correction for parasitic light is unnecessary in the conditions of our experiments.

Description of the Apparatus.

The apparatus is based on those described by Steubing²¹ and Mecklenburg.²² Special attention has been paid to the following points:—

(1) Objective measurement of the light intensities: this is made easy by the use of photo-electric cells of the *sperrschicht* type; we have chosen cells like those described by Bergmann²³ with high internal resistance (160 Ω) which were the more sensitive;

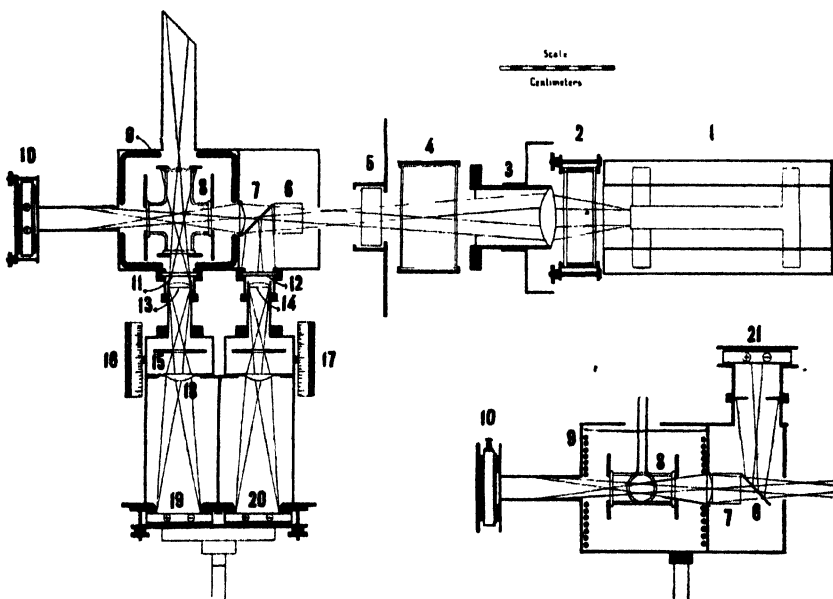


Fig. 1.

Fig. 2.

(2) use of monochromatic light, which commends itself for many reasons but especially because it allows accurate correction for the light absorption;

(3) avoidance of fluorescence by the use of a quinine sulphate solution absorbing the ultra-violet;

(4) avoidance of change in the state of polarisation of the light due to uncompensated reflections or refractions, especially in the path of the scattered light; this is important, even for comparative measurements, because two protein solutions may differ by the amount of the unpolarised light they emit. As will be seen from the following description, the only sources of the danger of inducing polarisation in our apparatus are the two glass plates providing the reference illumination (6 and 7 in Figs. 1 and 2); as, however, their planes of incidence are at 90° to each other, their influences are cancelled.

²¹ W. Steubing, *Ann. Physik*, 1908, **26**, 329.

²² W. Mecklenburg, *Kolloid Z.*, 1914, **14**, 172.

²³ L. Bergmann, *Physikal. Z.*, 1931, **32**, 286.

The apparatus is shown in horizontal section by Fig. 1 and a part of it in vertical section by Fig. 2. In the following description the numbers between brackets refer to the numbers on the drawing. As the apparatus is in fact a combination of several devices, it will be convenient to consider the following items separately.

(a) The Illuminating Device.

The quartz mercury vapour lamp (1) is enclosed in a double-walled cylinder, cooled by running water. Before leaving the apparatus this water passes through the cell (2) intended to protect the condenser lens, which otherwise may burst, because of the intense heat emitted by the lamp; if indeed the flow of water through cell (2) is momentarily stopped, the water in the cell will reach the boiling-point in a quarter of an hour. The quartz lamp is run at 65 volt, 3.7 amp. The condenser lens (3) has a diameter of 5 cm. and a focal length of 7 cm. and is equipped with an iris-diaphragm, whose opening is so regulated as to give a sharp beam of light in the cross-tube (8). The cell (4) contains the acid quinine sulphate solution. In (5) are placed the light-filters: these where the *monochromat* filters A and B of Zeiss, transparent respectively to the lines 5769-5790 Å. (yellow) and 5461 Å. (green). The light filters are placed behind a large diaphragm which avoids any stray light reaching the apparatus.

(b) The Cross-tube.

The cell containing the protein solution is a cross-tube as shown by Fig. 3. To the left is shown a horizontal section, to the right a front view of the assembled cell. The four plane glass windows are stuck on the end of the tubes by a little rubber grease; in front of each window is placed a blackened copper plate, provided with a hole somewhat smaller than the inside diameter of the tube; each pair of plates is joined by four bars, having screw-nuts at one end for pressing the glass windows on the tube and keeping everything together. Such cells are quite free of light scattering in the glass or reflections on irregularities; the volume element whose scattering is measured, shown on the drawing by the small rectangle around O, is distant from the entrance window, thus avoiding the anomalies observed by Mecklenburg²² in the vicinity of the plane of impact of the incident light.

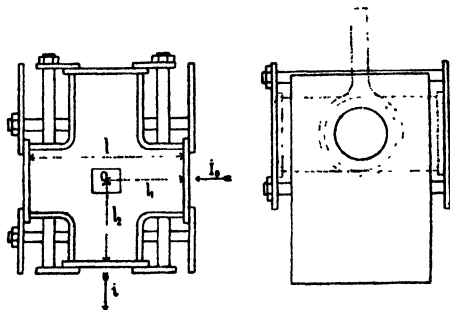


FIG. 3.

(c) Measurement of the Light-scattering.

The cross-tube is placed in the water-filled thermostat box, the temperature of which (27° C.) is controlled by circulating constant temperature water through the coil of copper tubing (9).

This box is provided with two tubes, one for catching the light emerging from the cross, the other for procuring a dark background to the scattering solution. Before entering this box a fraction of the incident light is reflected horizontally by a thin glass plate (microscope coverglass) (7) on to a diffusing screen (12) made of white paper and a piece of blue glass). The bulk of the light passes through a small lens which forms an image of the front window of the arc lamp in the centre of the cross-tube.

The measuring apparatus, strictly speaking, is composed of twin low power microscopes, whose objectives (13 and 14) fit into the sleeves of the windows (11 and 12). Objective (13), having 30 mm. focal length, forms an image of the diffusing beam on the square opening of the diaphragm (15); the lens (18) forms an image of the opening of objective (13) on the photoelectric cell (19). The opening of diaphragm (15) can be varied by turning the graduated drum (16). This diaphragm with its optical parts is the same as used in the Zeiss-Pulfrich photometer. The graduation of the drum is in hundredths of the amount of light which passes

the diaphragm at full aperture. The photoelectric cells (19 and 20) are both connected directly to the same galvanometer, with their poles in opposition. The galvanometer is a Zernicke type D (25 ohms coil resistance) placed at 3 m. from the scale. For making a measurement the diaphragm drum (16) is placed at a fixed graduation, and diaphragm drum (17) is adjusted till the galvanometer makes no deflection.

Let I_0 be the intensity of the unpolarised light incident upon the solution, i the intensity at unit distance of the scattered light emitted by a unit of volume of protein solution i' , and i_s the readings on the drums (16 and 17) respectively, V the illuminated volume of solution, and r its distance from the point of observation, then the *scattering power*, or the ratio i/I_0 is given by

$$\frac{i}{I_0} = K_1 \frac{i_s}{i_s'} \times \frac{V}{r^2} \quad (2)$$

K_1 is a proportionality factor dependent on the construction of the apparatus, and particularly on the sensitivity of the photoelectric cells (which is never the same for both and may vary with time), the transparency of the diffusing screen, the reflecting power and inclination of the glass plate (7), the transparency of the lenses, the windows and the thermostat water. Because these are variable and uncontrollable factors, it would be quite inaccurate to rely upon the constancy of the factor K_1 for comparative measurements not made immediately one after the other. For this reason a cube of opalescent glass of nearly the same scattering power as the protein solution has been used as a stable standard. (The cube used has 1.5 cm. edge length and has been prepared by Zeiss, Jena.) If the standard is substituted for the cross-tube containing the protein solution, without disturbing diaphragm (15), then both measurements are made under the same conditions, and if the two measurements are alternatively repeated until concordant results are obtained, the value of K_1 may be identical in the two cases.

We may write, as in equation 2,

$$\left(\frac{i}{I_0}\right)_s = K_1 \frac{i_s}{i_s'} \times \frac{V}{r^2}$$

As the diaphragm (15) has not been disturbed $i_s' = i_s$, and taking into account that $\left(\frac{i}{I_0}\right)_s$ is a constant, K_2 , depending only on the kind of glass used, one obtains, by combination of the last equation with equation 1,

$$\frac{i}{I_0} = K_2 \frac{i_s}{i_s} \quad (3)$$

The measured magnitude stands thus in a constant ratio to the scattering power, and is independent of the construction of the apparatus or of the conditions of operation. The values of i_s/i_0 are given in the table of results under the head: Relative scattering power.

(d) Measurement of the Light Absorption.

Because of the light absorption the intensity I_0 is not the one which reaches the point O (see Fig. 3), the centre of the volume element under consideration; because of its passage through a depth of solution l_1 (2.5 cm.) the incident light has been attenuated to the really effective intensity I and the ratio of the two intensities is given by

$$\log \frac{I_0}{I} = Kl_1.$$

Similarly the intensity i_0 of the light scattered by the point O is attenuated by its passage through a depth of solution l_2 (2.7 cm.) and

leaves the cross-tube with the intensity i , which is the one measured. Their ratio is given by

$$\log \frac{i_0}{i} = Kl_1.$$

Combining the two equations :

$$\log \frac{i_0}{I} \times \frac{I_0}{i} = K(l_1 + l_2).$$

The value of K is deduced from the measurement of the light absorption : to this end the apparatus is fitted with two photoelectric cells (10 and 21), one of which receives a fraction of the incident light, reflected on to it by the thin glass plate (6), the other, the light emergent from the cross-tube. These cells, shunted each by a 10-ohm resistance, are compensated against each other through a potentiometer bridge (100 ohms). Two readings are made, one with the cell filled with distilled water. If I_0 and I_1 are the intensities of the light emergent from the cell filled with water and with solution respectively and χ_w and χ the corresponding bridge readings, one may write, if l (5.2 cm.) is the total depth of the cross-tube,

$$K = \frac{1}{l} \log \frac{I_0}{I_1} = \frac{1}{l} \log \frac{\chi_w}{\chi}.$$

Combining the two last equations,

$$\log \frac{i_0}{I} \times \frac{I_0}{i} = \frac{l_1 + l_2}{l} \log \frac{\chi_w}{\chi}.$$

The dimensions of the cross-tube being thus that $l_1 + l_2 = l$, one finds finally

$$\frac{i_0}{I} = \frac{i}{I_0} \times \frac{\chi_w}{\chi} \quad . \quad . \quad . \quad . \quad . \quad (4)$$

This is true when the scattering volume is so small as to be comparable to a point. Comparison of the results obtained by a more general equation with the results given by equation 3 showed that the agreement was better than 1 per cent. in extreme cases. The correction factor for absorption, $\frac{\chi_w}{\chi}$, is to be found in the table of results.

Results.

Combining equations 1, 3 and 4 and assembling constants, we obtain :

$$\frac{\chi_w}{\chi} \times \frac{i_p}{i_0} \times \frac{I}{g} \times \frac{[\frac{n_2^2 - n_1^2}{n_2^2 + 2n_1^2}]^2 \times \frac{6(1+\rho)}{6-7\rho} \phi^2}{1} = KM.$$

In the table of results the values of the numerator of this fraction are collected under the heading : Specific relative scattering power. The values of the fraction should be a constant, independent of the protein concentration : from an inspection of the table it is evident that the values of KM show a distinct trend with increasing protein concentration. Because of this influence of the concentration one should not expect the KM values for two different proteins to stand in the ratio of their molecular weights. Moreover, the above equation is not accurate at finite concentrations ; it will, however, be correct if we replace the value of K at any concentration by its particular value K_0 at zero concentration.

K_0 is a true constant valid for all proteins. If then we divide the KM values for each protein by its molecular weight, we may expect all the K values to converge towards a single K_0 value at infinite dilution.

The result of this calculation is shown in Fig. 4. Three results (G_s and G_s for ovalbumin and D_s for haemocyanin) have been omitted

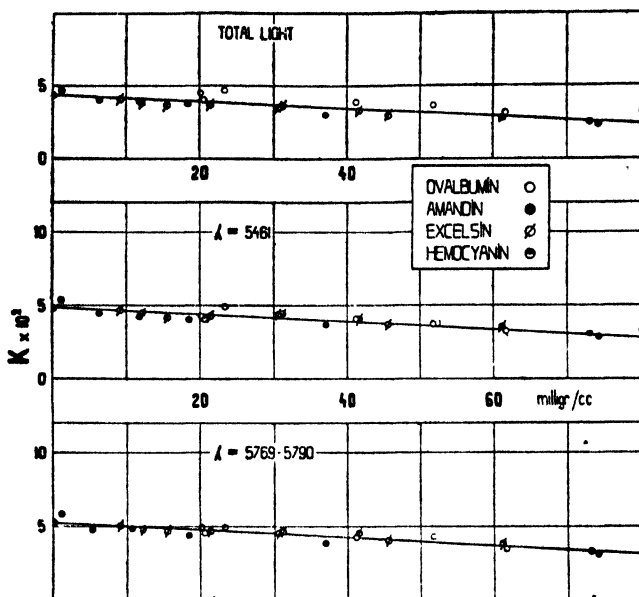


Fig. 4

because of their large discrepancy; they are listed, however, in the table of results which thus contains the complete series of our final experiments. Because of lack of space haemocyanin is represented in the diagram by two points only (highest and lowest value). It is at once clear that not only is the convergency towards a single K_0 value realised but even the concentration effect is the same for ovalbumin, amandin and excelsin, for which the points fall on the same line. The average divergence is, for the light of the yellow doublet, zero for excelsin, + 3.2 per cent. for ovalbumin and - 4.6 per cent. for amandin; it is likely that this larger negative discrepancy for amandin is due to the uncertainty of the refractive index which may be a trifle too high. The divergence is of the same order for the green wave-length; it is more pronounced for the total light, for which the absorption correction is more or less uncertain.

The precision of the results is therefore satisfactory and the convergence observed would be impossible if ionisation and hydration of the protein played a significant part in the light-scattering process, because neither the acidity nor the salt content of our preparations was fixed at a definite level, the p_H values given in the Table being only averages and the salt content varying from nearly half-saturation with ammonium sulphate to the concentration of a very dilute phosphate buffer.

Moreover, if there were a marked discrepancy between the molecular weight effective in the light-scattering and the values determined by Svedberg, the observed concordance would again not be realised.

We may therefore conclude that the main factor in the light-scattering of an isotropic protein is the molecular weight of the protein and that its scattering power is a true measure of its molecular dimensions.

Summary.

The purpose of this paper is to ascertain the relationship of the scattering power of a protein solution to the molecular weight of that protein. To this end solutions of ovalbumin, amandin, excelsin, and haemocyanin have been examined. It is shown that, if due attention is paid to the minor factors intervening in the scattering phenomenon, the scattering power stands exactly in the ratio of the molecular weights of these proteins; influences such as hydration and ionisation must play an insignificant rôle, if any.

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ON THE USE OF THE McLEOD GAUGE WITH NON-PERMANENT GASES.

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Although the use of the McLeod gauge with the permanent gases is unquestioned, some uncertainty appears to exist regarding the conditions under which it may be employed, if at all, with the non-permanent gases. Thus Reilly, Rae and Wheeler,¹ referring to the McLeod gauge, write: "It cannot, of course, be used for the non-permanent gases, owing to the non-applicability of Boyle's Law." Drucker and Proskauer² state: "It must be observed, that the partial pressures of non-condensable gases only can be measured." Finally, Dunoyer,³ after discussing disturbances in the readings due to the presence of water vapour and the vapour of organic substances, goes on to say: "Inexactitudes of this kind are produced even with gases such as CO₂."⁴ Similar statements by other authors might be quoted but these three, from books published in different countries, may serve to show how prevalent is this opinion.

On the other hand the McLeod gauge has been used to measure pressures of non-permanent gases down to very low values.⁵ In some cases remarkable theories have been propounded to explain the effects observed.

On account of the conflict of opinion revealed, it appears desirable to examine the question more closely. We shall see that departures from Boyle's law are not sufficiently serious to invalidate measurements of pressure made with the aid of the McLeod gauge and rarely necessitate

¹ J. Reilly, W. N. Rae, and T. S. Wheeler, *Physico-chemical methods*, 1926 edition, p. 381. The statement is repeated in the 1932 edition, p. 398.

² C. Drucker and E. Proskauer, *Physikalisch-chemisches Taschenbuch*, 1933, p. 90.

³ L. Dunoyer, *La technique du vide*, 1924, p. 75.

⁴ The writer has found no sign of abnormal behaviour with CO₂, if properly dried, over the pressure range discussed in the present paper.

⁵ Cf. M. Polanyi and K. Welke, *Z. physik. Chem.*, 1928, 132, 371.

even a correction being made. We shall further see that the real cause of the apparent failure of the gauge lies in the movements of sorbed gas between different parts of the system, which accompany the free gas displaced when the pressure is altered. These movements may be sufficient to vitiate conclusions based on the application of the gas laws to the known volumes and observed pressure changes.

Theoretical.

(a) Influence of Departures from Boyle's Law.

Over the pressure range with which we are here concerned the non-permanent gases are more easily compressible than a perfect gas. In the case of a real gas we may put

$$\frac{p_0 v_0}{p_1 v_1} = 1 + \lambda$$

where the suffixes 0 and 1 denote atmospheres pressure.

Within the limits of accuracy we require $p v$ may be considered linear over the whole range of p from 0 to 1.

If p_i is negligible compared with p_f , as is usually the case in the McLeod gauge, we may write, since λ is small,

$$p_i \simeq p_f \cdot \frac{v_f}{v_i} (1 + \lambda \cdot p_f)$$

where the suffixes i and f refer to the initial and final states of the gauge. Hence, in order to correct for departures from Boyle's Law, we must multiply the calculated values of p_i by a correction term $(1 + \lambda \cdot p_f)$.

At 0°C , λ for NH_3 is 0.01499 and for SO_2 0.02341; ⁶ at room temperature the values will be somewhat lower. Hence, in order that the correction for departures from Boyle's Law should amount to 1 per cent., the gas in the capillary chamber of the McLeod gauge would need to be measured at a pressure of ca 360 mm. Hg. in the case of SO_2 and ca 560 mm. Hg. in the case of ammonia. In practice measurements would almost certainly be made at reference marks involving appreciably shorter columns of mercury, so that the correction would be smaller.

(b) Sorption Effects.

There is, however, another property characteristic of the non-permanent gases which might be adduced to explain the alleged failure of the gauge; that is the readiness with which they are taken up by glass surfaces. It is generally assumed that the main effect takes place in the capillary compression chamber of the gauge, since only here does an appreciable pressure increase occur. In accordance with this view readings are usually taken at different points of the capillary. If the calculated pressures show no sign of diminishing as the volume is reduced from point to point, sorption effects are considered to be absent, or insignificant in amount. This conclusion is, however, open to criticism. True adsorption on a given surface is practically complete at very low pressures.⁷ The adsorption v . pressure curve rises steeply at first, bends

⁶ Values taken from Landolt-Bornstein.

⁷ See, for example, J. W. McBain, *The Sorption of Gases and Vapours by Solids*, 1932.

over sharply and approaches asymptotically a saturation value corresponding, in many cases, to a monomolecular layer. Bearing in mind the disproportion between the areas of surface involved and the fact that adsorption curves refer to quantities of gas at N.T.P., whereas the volume actually measured varies inversely as the pressure, we are forced to the conclusion that an appreciable proportion of the initially free gas may disappear before the rising mercury reaches the compression chamber and that the subsequent disappearance of gas may be too small to reveal itself in the readings taken from mark to mark of the capillary.

The sorption relationships on glass surfaces are more complicated than the simple case outlined above. Sorption is not reversible, and prolonged time effects, in some cases extending over years, may be observed. Consequently the quantity of gas sorbed on a given surface cannot be calculated from the instantaneous conditions of temperature and pressure; it depends also on the previous history of the system. Finally, the acid treatment to which an apparatus is usually subjected before or after erection leaves a layer of silica gel behind,⁸ so that the true surface available may be many times greater than the geometrical surface.⁹ A fair amount of experimental work has been done on this subject by workers interested in accurate gas measurements, notably by Burt¹⁰ and co-workers in England and by Moles¹¹ and co-workers in Spain. Applying the results of these authors to the problem of the change in sorption occurring in the McLeod gauge during the operation of taking a reading, the writer obtained a series of curves of the general shape indicated in the figure (Fig. 1). It may be observed that the general shape of the curves resembles that deduced qualitatively for true adsorption. In neither case can constancy of the readings taken at different points of the capillary be accepted as sufficient indication of the absence of sorption effects in the body of the gauge.

Experimental.

Readings of a McLeod containing an easily compressible gas, SO_2 , have been compared with readings of a similar gauge containing a permanent gas, air, at the same pressure.

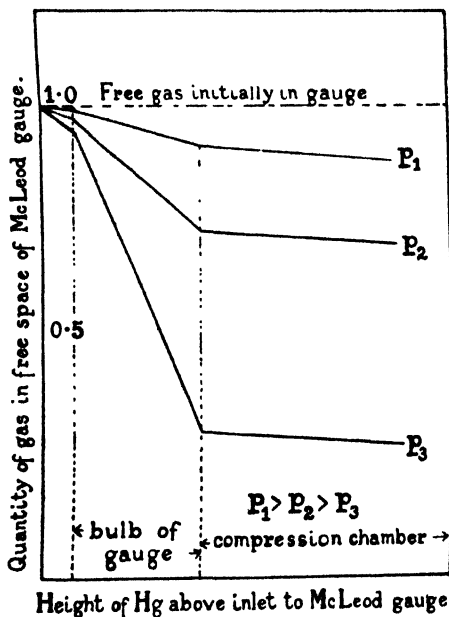


FIG. 1.

N.B.—For comparison purposes the free gas initially present in the gauge at each pressure has been taken as unity.

⁸ H. S. Frank, *J. Physic. Chem.*, 1929, **33**, 970.

⁹ I. Langmuir, *J. Am. C.S.*, 1916, **38**, 2283.

¹⁰ D. H. Bangham and F. P. Burt, *Proc. Roy. Soc., A*, 1924, **105**, 481; M. Francis and F. P. Burt, *Proc. Roy. Soc., A*, 1927, **116**, 586, etc.

¹¹ M. Crespie and E. Moles, *Anal. Soc. esp. fis. quim.*, 1926, **24**, 452.

The principle of the apparatus used is illustrated in the diagram (Fig. 2), which represents part of an apparatus given in greater detail elsewhere.¹² Self-evident accessories, such as drying tubes, condensation bulbs, tell-tale manometers, etc., have been omitted for the sake of clearness. During the experiments one gauge was reserved for the non-permanent gas, which was carefully excluded from the other. The sulphur dioxide employed was kept dry and free from traces of permanent gas by repeated distillations off P_2O_5 .

Over a certain pressure range the two gauge systems could be adjusted to the same pressure by the aid of the point "U" tube manometer M.

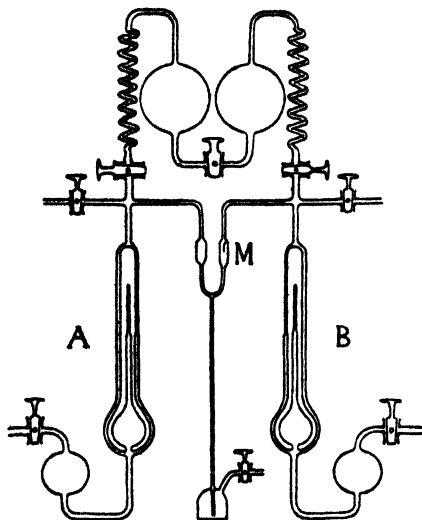


FIG. 2.

In the absence of thermostatic control settings of the point could not be relied upon to much less than 0.01 mm. Hg., so that it was useless attempting to compare pressures lower than 0.1 mm. by this method. For these gauges the buffer arrangement illustrated in the top half of the figure was employed, the "U" tube then serving merely to separate the two. Pressures in both systems were adjusted to approximately the same value before the communicating tap was opened. On opening the tap the large bulbs took up the gas displacement occurring during the pressure equalisation, while the long spirals prevented diffusion of air into the SO_2 gauge, or the contrary. Preliminary

tests with air in both sides demonstrated that pressure equalisation was rapidly complete, even at the lowest experimental pressures, and experience with different gases in the two gauges confirmed this.

A control on the results of the direct comparison experiments could be obtained by using the SO_2 McLeod gauge as a pipette, since its volume was known accurately, and allowing the contents to expand into a known volume. The ensuing pressure reduction could be compared with that calculated by the aid of the gas laws.

Results.¹³

(1) Comparison Experiments.

The comparisons effected by the intermediary of the point "U" tube manometer revealed complete agreement, within the limits of accuracy of the point setting. No particular interest attaches itself to giving the experimental figures for these pressures.

Some typical results of the comparisons made via the buffer system are given in Table I. The readings were taken randomly, but have been rearranged in descending order of pressures.

¹² M. Francis, *J. Physic. Chem.*, 1933, 37, 1019.

¹³ The experimental results quoted in this paper were obtained in the course of work carried out at Frankfurt-am-Main in the Summer of 1932.

TABLE I.—DIRECT COMPARISONS VIA THE BUFFER SYSTEM.

McLeod A. (SO ₂).	McLeod B. (Air).	Difference in Per Cent. on B.	Remarks.
mm. Hg.	mm. Hg.		
0.1058 ± 0.5	0.1038 ± 1.7	+ 2	After baking out
0.0237 ± 1.8	0.0238 ± 0.8	- 0.5	" "
0.0216 ± 1.1	0.0215 ± 1.3	+ 0.5	" "
0.0172 ± 2.1	0.0162 ± 1.0	+ 6.2	After sorbing at 125 mm. pressure
0.0148 ± 2.5	0.0144 ± 1.3	+ 3.0	After baking out
0.0129 ± 1.5	0.0127 ± 1.5	+ 1.6	After sorbing at 186 mm. pressure
0.0106 ± 3.7	0.0104 ± 0.9	+ 2.0	" " 125 mm. "
0.0099 ± 3.2	0.0097 ± 1.5	+ 2.0	" " 55 mm. "
0.0080 ± 2.6	0.0079 ± 1.4	+ 1.3	" " 55 mm. "
0.0078 ± 1.2	0.0075 ± 0.6	+ 4.0	After baking out
0.0074 ± 1.0	0.0074 ± 3.0	nil	" "
0.0041	0.0043	- 4.9	" "
0.0010 ₈ ± 1.2	0.0009 ₈ ± 4.0	+ 10	After sorbing at 186 mm.
0.0009 ₈ ± 7	0.0007 ₈ ± 3.0	+ 14	" " 125 mm.

The length of the compression chamber at the highest mark ¹⁴ was 13 mm. and a column of 10 mm. Hg. was equivalent to an initial pressure of 0.0015 mm. Hg. Assuming an accuracy of reading of the meniscus of 0.2 mm., the observational error at 0.001 mm. Hg pressure should not exceed ± 3 per cent. The observed differences at the lowest pressures were appreciably greater than this and were in the opposite sense to that anticipated; *i.e.*, instead of the SO₂ McLeod giving lower pressures than the gauge containing air, there seemed to be a general tendency for it to yield higher values. After standing overnight at a relatively high pressure of SO₂, the effect was found to be enhanced. This observation furnishes the clue to the explanation we advance tentatively. Before the series of measurements reproduced in Table I. was made, the gauge had been in contact with SO₂ at appreciably higher pressures for a considerable period; so that we were now working, on the whole, on the desorption side of the life-history of the system. During the experiments there was a continuous but slow release of sorbed gas, temporarily increased after the intermittent periods of resorption.¹⁶ Since both gauges were closed as nearly as possible simultaneously on taking a reading, the difference between the two indicates the amount of sulphur dioxide liberated by the walls of the gauge containing this gas, before they were submerged in the rising mercury. That gas was being released was evident from the slow initial rise in the reading furnished by both gauges after the pressure equalisation was complete. The source of the released gas was checked by isolating the gauges and following the subsequent change in each separately. It was repeatedly observed that a slow release of gas took place in that part of the system containing SO₂, independently of the direction of flow of gas in the pressure equalisation.

Although it cannot be doubted that release of sorbed gas was responsible for part of the difference observed between the readings of the two gauges, it is possible that the readings of the gauge containing AIR were too low, an imperceptible oxide film ¹⁸ flattening slightly the meniscus in the

¹⁴ The highest reference mark must be far enough from the sealed end to avoid the necessity of setting the mercury at a point of the capillary, which has been heated in the flame. At such points the capillary depression of the meniscus is liable to be abnormal.

¹⁸ The initial pressure adjustments were made in the gauge systems alone, the large globes of the buffer system being exhausted, so that the gauges were for a time in contact with gas at about 15 times the final pressure.

compression chamber. In this case the McLeod containing SO_2 was behaving better than we have supposed.

(2) Distribution Experiments.

Some typical results of distribution experiments between the McLeod gauge system and a reservoir of some $1\frac{1}{2}$ litres capacity (not shown in the figure) are given in Table II.

TABLE II.—DISTRIBUTION EXPERIMENTS.

Initial Pressure.		Final Pressure.		Per Cent. Error on Calculated Pressure.	Remarks.
Reservoir.	McLeod.	Observed.	Calculated.		
mm.	mm.	mm.	mm.	mm.	
1.518	2.612	1.724	1.724	Nil	No appreciable change with time
1.248	0.0188	0.8728	0.8743	- 1.7	" " "
0.4581	0.0187	0.3234	0.3245	- 0.4	" " "
0.2265	0.0149	0.1589	0.1622	- 2.1	Changed less than 1 % in 21 hours
0.0674	0.1892	0.0906	0.0903	+ 0.3	" " " 1 % " 18 "
0.0450	0.1669	0.0684	0.0679	+ 0.7	" by 1.5 % in 1 hour "
0.0224	0.1418	0.0455	0.0448	+ 1.5	20 mins. after distributing
		0.0450	0.0448	+ 0.4	55 " " "
0.0191	0.0001	0.0143	0.0133	+ 7.5	18 " " "
		0.0098	0.0100	- 2.0	50 " " "
0.0143	0.0001	0.0105	0.0100	+ 5.0	23 hrs. " " "
0.0105	0.0010	0.0072	0.0081	- 12.5	15 mins. " " "
0.0072	0.0012	0.0051	0.0054	- 5.6	40 " " "
		0.0037	0.0031	+ 18.9	10 " " "
nil	0.0169	0.0031	0.0031	- 0.3	23 " " "
		0.0031	0.0031	- 2.2	78 " " "
0.0045	nil	0.0028	0.0034	- 17.1	20 " " "
0.0039	0.0000	0.0018	0.0022	- 22.4	20 " " "
		0.0005	0.0005	- 15.2	25 " " "
nil	0.0031	0.0004	0.0005	- 20.3	55 " " "
		0.0006	0.0005	+ 10.2	18 hrs. " " "

Here, too, agreement was excellent at the higher pressures, whereas at the lower pressures serious discrepancies were observed.

Comparison of Tables I. and II. shows that the discrepancies set in at appreciably higher pressures in the distribution experiments. Moreover, the sign of the discrepancy appears to depend on the condition of the distribution, *i.e.*, on whether the pressure in the McLeod or that in the reservoir was initially the higher. To what extent desorption in one part of the system compensated for increased sorption in another depends on the pressure changes and surface areas involved, and on the previous history of the different sections. Owing to slow background effects an initial net loss of free gas might be changed into a gain on standing.

That sorption experiments were brought more strongly into evidence in the distribution experiments is due to the fact that in them we were concerned not only with pressures but also with quantities of gas. In the direct comparison experiments the quantity of gas in the system was immaterial, pressures alone were of interest. Moreover, the anticipated sorption effect, namely, too low a reading given by the McLeod measuring pressures of SO_2 , was not observed within the pressure range examined; if present it was masked by the overall desorption responsible for the slow upward drift of the readings after the pressure equalisation was complete.

Conclusion.

From the foregoing it is evident that pressure readings of sulphur dioxide obtained by the aid of the McLeod gauge are not seriously in error within the range here examined (lower limit ca 0.001 mm.). Such pressure readings may safely be used to characterise the state of a system for any purpose where the quantity of gas in the system is immaterial. Owing to uncertainties regarding the amount of sorbed gas it is not safe to combine pressure readings with volumes in order to determine quantitatively movements of gas to or from the system, or between its different parts. Since the sorbed gas plays an increasingly important rôle the lower the pressure, extreme caution should be exercised in the interpretation of phenomena observed at low pressures.

Summary.

1. Departures from the perfect gas laws (Boyle's Law) have been shown to be insufficient to account for the alleged failure of the McLeod gauge to measure pressures of non-permanent gases.

2. From general considerations it is shown that the main disappearance of gas by sorption on the walls during the taking of a reading may be expected to occur in the bulb of the gauge and not, as is generally assumed, in the capillary. Consequently, good agreement in the readings taken at different points of the capillary is not a sure indication that sorption errors are absent.

3. Direct comparison of the readings of a McLeod gauge containing SO_2 with those of a similar gauge containing air at the same pressure failed to reveal any serious discrepancy down to pressures of a few thousandths of a millimetre of Hg.

4. Owing to movements of sorbed gas when the pressure is changed in the system, it is not safe to combine observed pressure changes with known volumes in order to calculate quantities of gas transferred. Since the effect is greater the lower the pressure caution must be exercised in the interpretation of phenomena observed at low pressures, whatever method be adopted in the pressure measurement.

THE ATMOSPHERIC CORROSION AND TARNISHING OF TIN.

By L. KENWORTHY, M.Sc., A.R.C.S., A.I.C.

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I. Introduction.

Much of the value of tin as a metal and as a constituent of alloys depends on its resistance to corrosion and tarnishing. The good qualities of tin in this respect are recognised in many of its uses, but little quantitative information has hitherto been available on the rate of corrosion of tin under atmospheric conditions. Although a wide range of materials has previously been studied by Vernon,^{1,2} and Hudson,³ in the Atmos-

¹ First (Experimental) Report to the Atmospheric Corrosion Committee by W. H. J. Vernon, *Trans. Faraday Soc.*, 1924, 19, 839-934.

² Second (Experimental) Report to the Atmospheric Corrosion Committee by W. H. J. Vernon, *ibid.*, 1927, 23, 113-204.

³ Third (Experimental) Report to the Atmospheric Corrosion Committee by J. C. Hudson, *ibid.*, 1929, 25, 177-252.

pheric Corrosion Research of the British Non-Ferrous Metals Research Association, tin was not included. The present paper describes the extension of this work to the study of tin, the methods of testing adopted being essentially the same as those which were used in the earlier work.

The tests were carried out on samples, in the form of sheet and wire, of pure tin and tin alloyed with antimony and with copper. In order to preserve continuity with the previous work, however, and to provide a means of assessing the true value of tin, comparison samples of a few typical non-ferrous metals, whose behaviour under these conditions is now known, were exposed side by side with the tin samples.

A. Materials Tested and Method of Testing.

The methods of test employed were briefly as follows :—

1. Indoor Weight Increment Tests.—The increase in weight of plate specimens exposed indoors was determined periodically, using special refinements in the method of weighing.

2. Stevenson Screen Tests (Weight Increment Tests). Measurements of the increase in weight were made on small coils of 18 S.W.G. wire when exposed in a Stevenson Screen, giving conditions of outdoor exposure but entirely sheltered from rain. Weighings were made periodically throughout the test, thus giving a continuous record of the progress of corrosion.

3. Loss in Weight Tests.—Loss in Weight tests were applied to plate specimens subjected to complete exposure outdoors.

4. Tensile Tests.—The effect of complete exposure outdoors on the breaking load and percentage elongation of 18 S.W.G. wire specimens was measured.

Since the supply of available material did not permit of all the comparative materials being submitted to each test, a complete list of the materials and the methods of testing applied to each is given in Table I. The pure tin used, from which the two alloyed tins were also prepared, had the following analysis: Pb 0.0070; Fe 0.0030; Sb 0.0025; Bi 0.0017; S 0.0008; Cu 0.0004.

B. Conditions of Exposure.

The outdoor exposure stands were placed in the grounds of Birmingham University, facing approximately south-west. The position was fairly exposed, and the pollution was for the most part of the year considerable, since prevailing winds carried smoke towards the specimens from several large factory chimneys situated from a half to one mile from the exposure

TABLE I.—LIST OF MATERIALS TESTED AND METHODS OF TESTING.

Material.	Method of Testing Employed.
<i>Tin and Tin Alloys.</i>	
Pure Tin	1, 2, 3, 4
Antimonial Tin (Pure Tin + 2.2 per cent. Antimony)	1, 2, 3, 4
Cupriferrous Tin (Pure Tin + 0.2 per cent. Copper)	1, 2, 3, 4
<i>Comparison Materials.</i>	
H.C. Copper	1, 2, 3, 4
Brass (70 per cent. Copper; 30 per cent. Zinc)	3
Nickel	2, 3
Zinc	1, 3
Cadmium	1, 3, 4

site. The indoor exposures were conducted in the main Metallurgy Research Laboratory of the University of Birmingham, the atmosphere of which was, on the whole, fairly free from acid fumes.

II. Indoor Weight Increment Tests.

Indoors a record of the rate of tarnishing of the materials was obtained by measuring periodically the increase of weight of exposed specimens. The weighings were conducted on an accurate balance, using Conrady's modification of the Gaussian method of exchange.⁴ By this means it was possible, on specimens weighing about 70 grams, to weigh to an accuracy of at least 0.01 mg. Since an appreciable buoyancy effect is introduced by the difference in density between the tin specimens and the brass weights, an appropriate correction for the effect of temperature and barometric pressure was applied to each weighing.

A. Rate of Tarnishing of Tin and Tin Alloys.

Duplicate specimens of the three materials, 10 cms. \times 5 cms. \times 2 mms. thick were exposed for this investigation, each plate being suspended vertically from a stand, by two tinned copper wire hooks passing through holes drilled in the corners of the 5 cms. edge. To prevent dust from settling on the plates, horizontal covers, 3 inches wide, were placed immediately above. The only treatment which the plates received, after preparation and before the initial weighing, was a rinsing in acetone to remove grease. Periodical weighings were carried out during the first 14 months and finally after 25 months.

Very little change was detected in the appearance of the plates for quite a considerable time. After 100 days' exposure there was a slight dulling of the surface and close inspection with the aid of a lens revealed a number of small white tarnish spots, these being slightly more pronounced on the antimonial tin. After 150 days a noticeable tarnish had developed. This took the form of a faint yellow grey film when the plates were viewed at an angle near the normal and a bluish grey bloom when viewed by light reflected at a very oblique angle. This tarnish increased gradually on all the specimens to the end of the exposure. The antimonial tin appeared to be slightly the worst in this respect, but the difference was hardly detectable.

The results of the periodical weighings are given in Table II. As might

TABLE II.—INDOOR WEIGHT INCREMENTS OF TIN AND TIN ALLOYS.

Exposure in Days.	Weight Increments in Milligrams. (Surface Area of each Specimen = 1 sq. decimetre.)								
	Pure Tin.			Tin + 0.2 per cent. Copper.			Tin + 2.2 per cent. Antimony.		
	Specimen 1.	Specimen 2.	Mean.	Specimen 1.	Specimen 2.	Mean.	Specimen 1.	Specimen 2.	Mean.
12	0.102	0.048	0.075	0.073	0.088	0.081	0.109	0.105	0.107
32	0.130	0.125	0.128	0.130	0.179	0.155	0.092	0.124	0.108
56	0.333	0.223	0.278	0.274	0.307	0.321	0.317	0.349	0.333
83	0.332	0.297	0.315	0.355	0.429	0.392	0.350	0.436	0.393
111	0.464	0.418	0.441	0.431	0.533	0.492	0.398	0.442	0.420
145	0.597	0.561	0.579	0.727	0.717	0.722	0.706	0.713	0.710
200	0.994	0.941	0.968	1.115	1.124	1.120	1.120	1.116	1.118
258	1.108	1.083	1.096	1.340	1.345	1.343	1.375	1.380	1.378
368	1.172	1.164	1.168	1.491	1.568	1.530	1.606	1.634	1.620
763	2.619	2.638	2.629	3.057	3.161	3.109	3.259	3.299	3.279

⁴ A. E. Conrady, *Proc. Roy. Soc.*, 1922, 101A, 211.

be anticipated, there was very little difference between the rates of attack of the three materials, the variation being 0.65 mg./dm.² after 763 day's exposure. Consequently an attempt to discuss their relative merits must

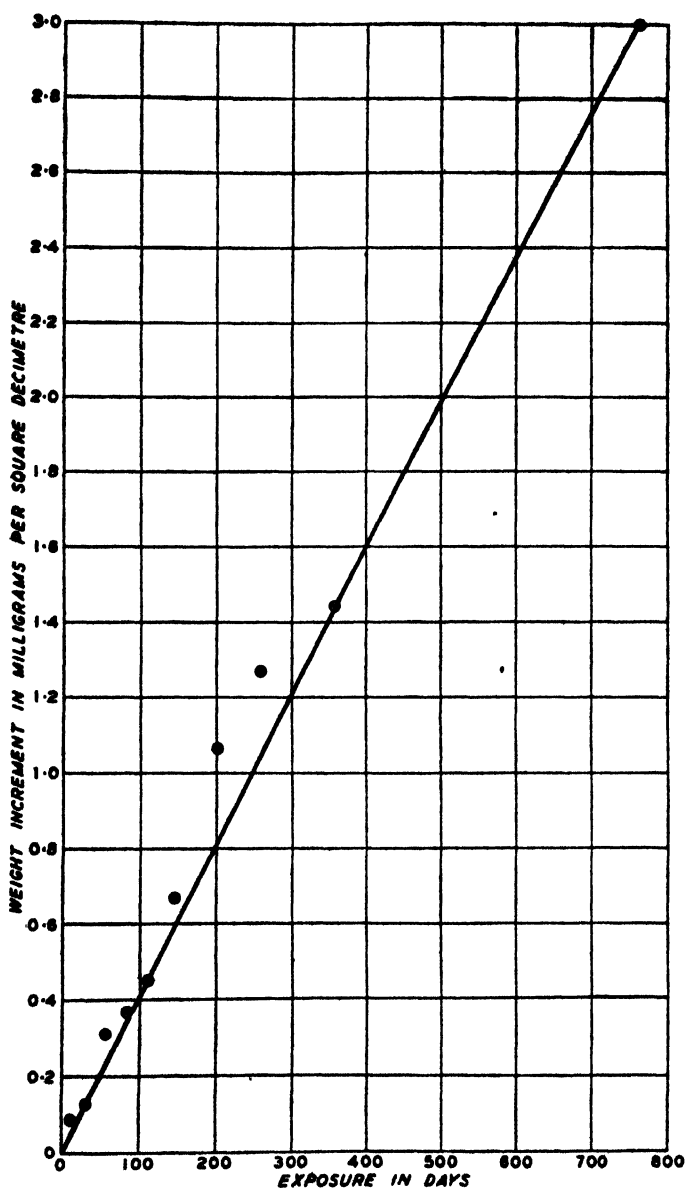


FIG. 1. WEIGHT INCREMENT OF TIN IN AN INDOOR ATMOSPHERE.

be approached with some caution. The results would seem to indicate, however, that refinement of the metal increases its corrosion resistance. In Fig. 1, the average weight increments obtained for the three materials are plotted against time of exposure, and the relationship is seen to be linear

except for slight fluctuations due to variations in the atmospheric conditions. Thus tin with a rolled surface as supplied by the manufacturer tarnishes at a slow but uniform rate, and if there is any surface film present it is not of a completely protective nature.

B. Influence of Surface Condition on the Rate of Tarnishing of Tin.

The object of these tests was to determine the rate of tarnishing of specimens exposed with a perfectly clean metal surface. This was prepared by scraping the specimens under acetone with a safety razor blade. Immediately following scraping, the specimens were brushed with a camel hair brush to remove particles of abraded metal and then transferred rapidly to a vacuum desiccator which was at once evacuated by an oil pump. Removal of all air from the desiccator was ensured by filling with nitrogen from a cylinder and re-evacuating. The plates were then left at the side of the balance overnight before weighing. Plates of only 1 mm. thickness were employed in these tests thereby enabling the surface area to be doubled (to 10 cms. \times 10 cms.) without increase of weight.

Four plates of each material were exposed, two with the specially prepared surface and two with the manufacturer's surface. The results of periodical weighings of these twelve plates are given in Table III. It will be noticed that the three materials in either surface condition are in close agreement and show no evidence of any difference in the degree of attack.

TABLE III.—INDOOR WEIGHT INCREMENTS OF THREE VARIETIES OF TIN, EACH EXPOSED WITH 2 DIFFERENT SURFACE CONDITIONS. (SURFACE AREA OF EACH PLATE = 2 SQ. DECIMETRES.)

MANUFACTURER'S SURFACES.						SCRAPED SURFACES.					
Pure Tin.		Antimonial Tin.		Cupriferrous Tin.		Pure Tin.		Antimonial Tin.		Cupriferrous Tin.	
Ex- posure (Days).	Mean Wt. Inc. of 2 Plates (Mgms.).	Ex- posure (Days).	Mean Wt. Inc. of 2 Plates (Mgms.).	Ex- posure (Days).	Mean Wt. Inc. of 2 Plates (Mgms.).	Ex- posure (Days).	Mean Wt. Inc. of 2 Plates (Mgms.).	Ex- posure (Days).	Mean Wt. Inc. of 2 Plates (Mgms.).	Ex- posure (Days).	Mean Wt. Inc. of 2 Plates (Mgms.).
						0.2	0.138	0.1	0.115	0.1	0.114
						1	0.256	1	0.155	1	0.130
2	0.035	2	0.021	2	0.008	2	0.304	2	0.152	2	0.150
4	0.105	4	0.049			4	0.301	4	0.156	4	0.182
7	0.114	7	0.062	7	0.019	6	0.303	6	0.174	6	0.172
11	0.120	12	0.087					12	0.170	14	0.375
18	0.147					18	0.368	18	0.336		
36	0.352	32	0.255	27	0.141			30	0.471	27	0.437
67	0.516	65	0.527	60	0.387	49	0.662	60	0.678	58	0.659
96	0.721	93	0.672	88	0.584	76	0.912	90	1.014	85	0.976
126	0.882	123	0.824	118	0.704	107	1.071	121	1.159	116	1.125
156	1.176	153	1.160	148	0.982	137	1.362	151	1.400	146	1.383
184	1.386	181	1.341	176	1.147	166	1.635	180	1.689	175	1.678
240	1.997	237	1.857	232	1.690	222	2.426	236	2.541	231	2.414
304	2.422	301	2.294	296	2.164	286	2.888	300	3.175	295	2.941
792	5.279	789	5.392	785	5.319	775	5.547	789	6.406	784	5.701

A further test to determine more accurately the initial portion of the weight increment/time curve was carried out using 8 plates of the pure tin, 10 cms. \times 5 cms. \times 2 mms. thick. Before exposure they were treated by scraping under acetone as described above. The average values of the

weight increments of the 8 plates are plotted against time of exposure in Fig. 2.

The increase in weight of these plates during the first 24 hours' exposure was very rapid, corresponding with about 4 weeks' exposure of a manufacturer's surface. The increase was at first so rapid that it could be detected during the course of the initial weighing.

After 24 hours, however, a rapid flattening of the curve towards the time axis occurred, and the weight remained almost constant for about 8 days, when another sudden although smaller increase took place, finally merging into the steady linear relationship observed with the manufacturer's surface. The mechanism of these changes has not been further investigated. The first portion of the curve, however, would suggest the formation

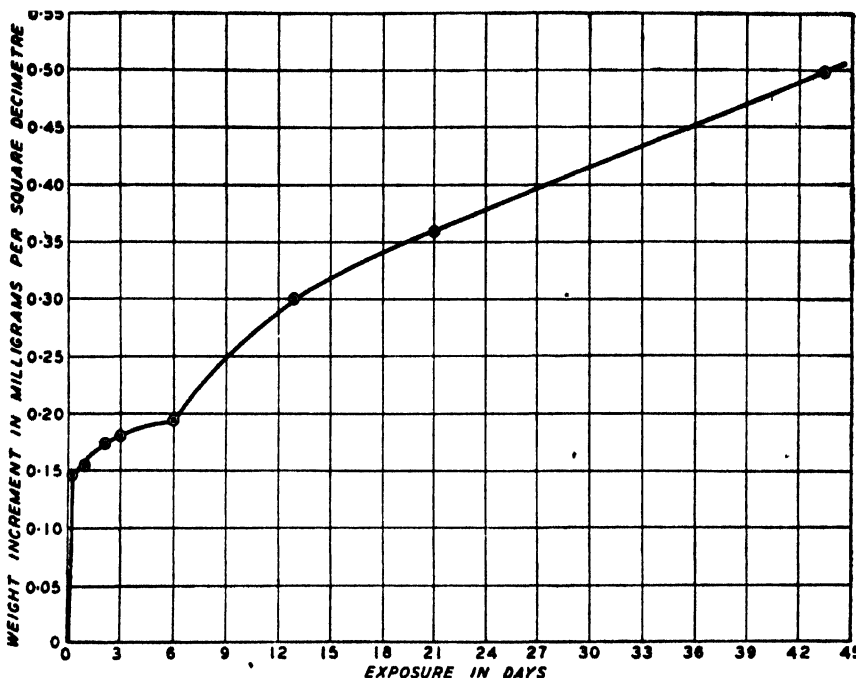


FIG. 2. INITIAL PORTION OF THE WEIGHT INCREMENT/TIME CURVE OF TIN WITH A SPECIALLY PREPARED CLEAN SURFACE, EXPOSED TO AN INDOOR ATMOSPHERE.

of an impervious film, whilst the secondary sudden increase seems to indicate a fresh attack caused by the rupturing of this film or by its change to a more pervious one, similar, if not identical with that existing on the manufacturer's surface.

C. Comparison of the Rate of Tarnishing of Tin with that of Other Non-Ferrous Metals.

For this investigation, duplicate specimens of the pure tin, copper, zinc and cadmium were employed. With the exception of the tin, which was exposed in the "as received" condition except for a rinsing in acetone, the plates were treated with Hubert No. 1 emery paper, followed by cleaning with cotton wool soaked in acetone. They were then transferred to a vacuum desiccator and allowed to stand in vacuo overnight before the initial weighings. The weight increments of these specimens are plotted against time of exposure in Fig. 3.

It will be seen that the curves obtained for copper and cadmium were parabolas and those for zinc and tin, straight lines, the copper and zinc lines being in close agreement with the work of previous investigators (Vernon^{1,2} and Patterson³). Under these conditions, tin resisted attack more than copper, zinc and cadmium, the relative weight increments in milligrams after 220 day's exposure being: tin 100, copper 178, zinc 357 and cadmium 488.

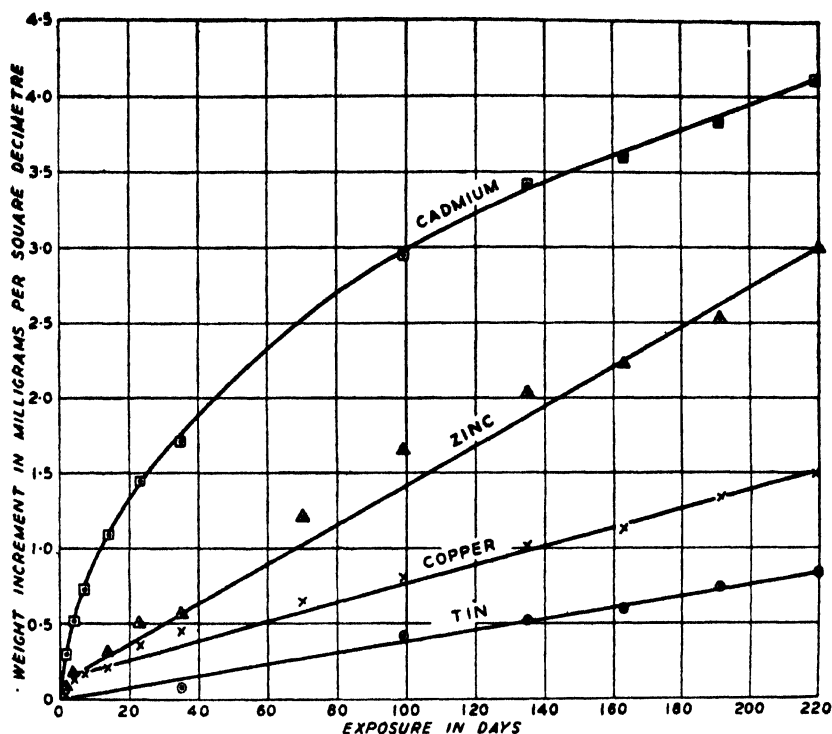


FIG. 3. COMPARISON BETWEEN TIN AND OTHER METALS IN AN INDOOR ATMOSPHERE WEIGHT INCREMENT TESTS.

III. Stevenson Screen Tests.

This method, which is fully described in the Third (Experimental) Report to the Atmospheric Corrosion Committee,³ consists in exposing coils of wire in a Stevenson Screen, where they are subjected to a current of air but sheltered from direct rainfall, corrosion being determined by the increase in weight of the coils.

Eight coils of each of the three varieties of tin were exposed and for comparison eight coils of copper and four of nickel, each coil consisting of approximately 2 metres of 18 S.W.G. wire.

Weighings were conducted at first every fortnight, subsequently every 4 weeks and finally at 8-week periods, up to a total period of exposure of 52 weeks. The actual duration of the test, however, including the time during which the specimens were in the laboratory, was 14 months.

³ W. S. Patterson, *J. Electroplaters' and Depositors' Tech. Soc.*, 1930, 5, 91.

Results.

(a) **Visual.**—The pure tin and the tin containing copper exhibited small patches of yellow corrosion product after a fortnight's exposure. Later they assumed a mottled grey appearance, and the corrosion product had a tendency to exfoliate. The antimonial tin behaved quite differently. After a few weeks, the specimens showed a number of black spots, although the general appearance remained quite bright. The spots eventually developed into dark grey patches, only one coil exhibiting any trace of yellow. After the year's exposure, they showed as a whole the least attack of any of the specimens, most of the coils retaining some reflectivity. The corrosion product was detached only with difficulty.

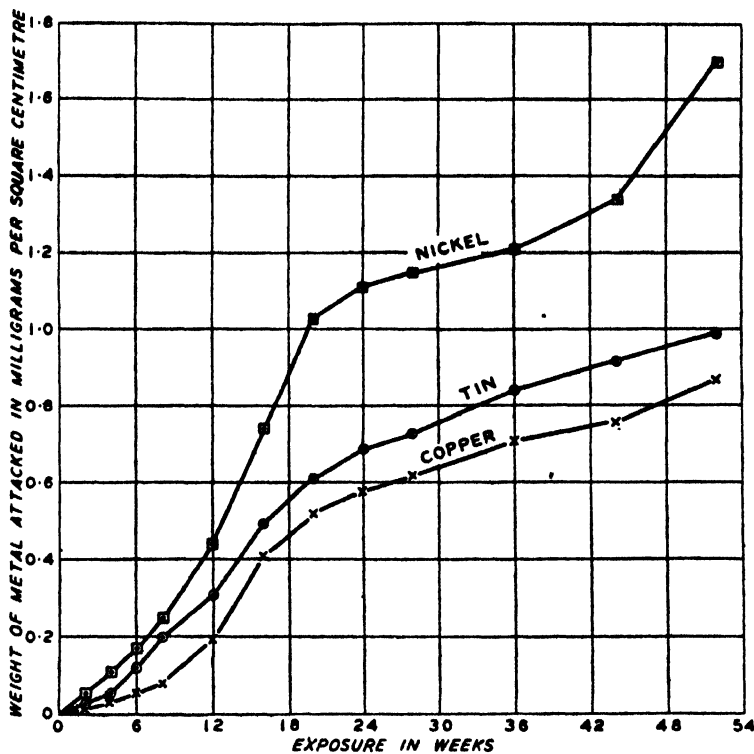


FIG. 4. STEVENSON SCREEN TESTS.

(b) **Gravimetric.**—In order to render the results strictly comparative, the weight of metal attacked at each stage of the exposure has been calculated for each material, from the analysis of the corrosion products, these values being plotted against time of exposure in Fig. 4. The tin line represents the average value of the three varieties of tin, since the differences between them were extremely small.

Under Stevenson screen conditions it will be noticed that copper proved slightly more resistant to attack than tin, whereas nickel showed considerably more attack than either of these.

Attack under these conditions has been shown to be influenced to a large extent by the deliquescence of the corrosion products in relation to the humidity of the atmosphere. Since the specimens are shielded from rain, the corrosion products remain in contact with the metal. Consequently those materials which form deliquescent corrosion products, tend to corrode the most.

An experiment was therefore carried out to test the deliquescent nature of the corrosion products detached from the specimens after the year's exposure. Fig. 5 shows the increase in weight of the corrosion products, due to condensation of water vapour, as the humidity rises. It will be seen from these curves that the deliquescence of the corrosion products is in close agreement with the rates of attack of the corresponding materials in the Stevenson screen.

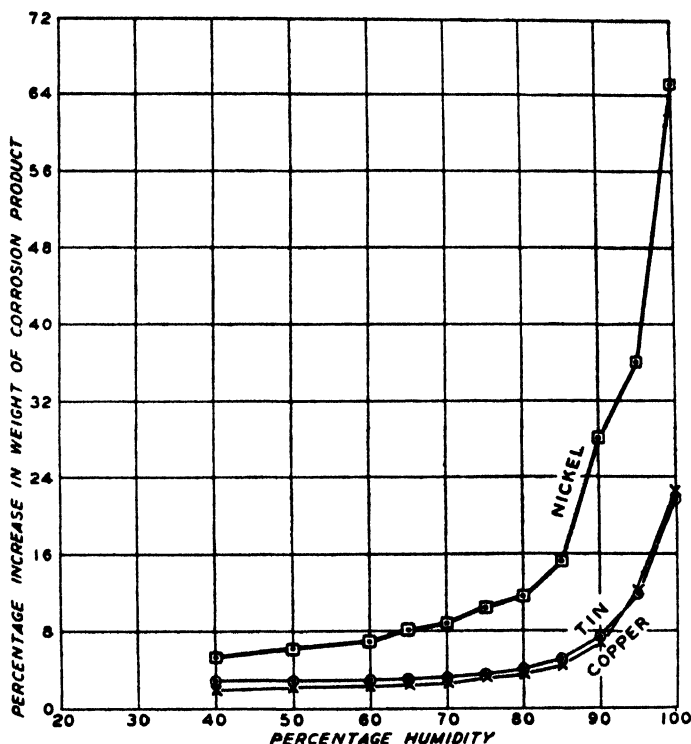


FIG. 5. PERCENTAGE INCREASE IN WEIGHT OF CORROSION PRODUCTS FROM SCREEN TESTS, AFTER EXPOSURE FOR SUCCESSIVE PERIODS TO ATMOSPHERES OF INCREASING HUMIDITY.

IV. Outdoor Loss in Weight Tests.

The three samples of tin were subjected to outdoor Loss in Weight Tests, together with specimens of H. C. copper, nickel, zinc and cadmium, for comparison. Each material was represented by duplicate plates, 10 cms. \times 5 cms. in area \times 2 mms. thick in the case of the tin specimens and 1 mm. thick in the case of the other materials. Except for a rinsing in acetone, the specimens were exposed as received from the manufacturers. After the initial weighings, the plates were suspended vertically by pieces of string passing through holes in the corners and fixed to hooks on the exposure stand.

Results.

(a) **Change in Appearance of the Tin Specimens.**—All the plates, following a slight fall of rain, quickly assumed a mottled white appearance,

but subsequent changes were very gradual. It was impossible to make any distinction between the different grades until they had been exposed for about four months. The antimonial alloy was then noticed to have lost more reflectivity than the other two materials. At the conclusion of the exposure, which lasted 1 year, the general appearance of the plates was that of a dark grey background on which white spots were superimposed. The pure tin and the tin containing copper were somewhat lighter in colour than the antimonial alloy and still retained a slight reflectivity.

(b) **Calculation of Loss in Weight.**—The plates were first weighed as removed from the exposure stand, without any treatment. They were then cut up by a "guillotine" into two parts, the larger part, which was approximately $\frac{3}{4}$ of the whole plate being used for the loss of weight determination, whilst the smaller part was reserved as a specimen. Each portion was weighed separately, and in most cases there was a small loss in weight on cutting of the order of 1 or 2 mgms. which was corrected for in the loss of weight determinations.

In the case of the tin specimens it was found necessary to adopt a special method for the determination of the loss in weight on account of the softness of the metal. No suitable reagent was discovered for removing the corrosion product, which consisted mainly of stannic oxide and hydrated stannous oxide, without attacking to an appreciable extent the metal itself. The total amount of adhering product was also so small, that whilst it was essential to effect its complete removal, a certain amount of abrasion of the underlying metal was unavoidable. Difficulty in this operation had been anticipated at the commencement of the tests and extra plates had been exposed for the purpose of making preliminary experiments. The method which was evolved from these tests consisted in a very careful scraping of the plates by means of an ordinary pocket knife, or a safety razor blade, the whole of the corrosion product being removed with the minimum amount of abrasion of the metal. Separation of the free metal was done by a levigation process in a small test tube containing acetone. After pouring off most of the corrosion product, the remaining portion, which consisted of particles of tin with a small amount of adhering corrosion product, was then transferred to a weighed porcelain crucible, treated with a few drops of concentrated nitric acid and ignited to constant weight as stannic oxide. The difference in weight obtained was due to the weight of oxygen which had combined with the free metal, since change in weight of traces of corrosion product adhering to the metallic particles was negligible. The weight of the abraded metal thus determined was subtracted from the loss of weight of the plate after scraping. This procedure was carried out separately for both sides of the plate.

The plates of the comparison materials were scraped in the same way as the tin plates, with practically no abrasion of the metal, until only a thin dull film remained. This was removed by scrubbing the plates for a few seconds with a small nail brush in a suitable reagent. A 10 per cent. solution of acetic acid was used for the zinc and cadmium plates, a 1 per cent. solution of hydrochloric acid for nickel and a 10 per cent. solution of 0.880 ammonia was employed for the copper and brass plates. These reagents have been used and found suitable in previous work of a similar nature.*

A summary of the results obtained is given in Table IV. The change in weight of the specimens after exposure is given in Column A and the corrosion product adhering to the plates is shown in Column B. The algebraic difference B — A, gives the weight of metal corroded and is given in Column C.

Discussion of Results.

The three varieties of tin behaved very similarly in their resistance to attack outdoors and the differences between them were not sufficient to

* J. C. Hudson, *J. Electroplaters' and Depositors' Tech. Soc.*, 1929, 25, 221.

TABLE IV.—OUTDOOR LOSS IN WEIGHT TESTS. 1 YEAR'S EXPOSURE. COMPARISON OF TIN AND TIN ALLOYS WITH OTHER NON-FERROUS MATERIALS.

Material.	Loss or Gain in Weight after Exposure. Mgms./dm ² .		Corrosion Product Removed by Scraping. Mgms./dm ² .		Weight of Metal Corroded. Mgms./dm ² .	
	(A.)		(B.)		(C.)	
		Mean.		Mean.		Mean.
Pure Tin . .	+ 70 + 62	+ 66	185 170	177	115 108	111
Antimonial Tin .	+ 47 + 44	+ 46	154 162	158	107 118	112
Cupriferos Tin .	+ 69 + 69	+ 69	198 194	196	129 125	127
Nickel . .	- 190 - 193	- 192	124 104	114	314 297	306
H. C. Copper .	- 26 - 21	- 23	291 291	291	317 312	314
70/30 Brass .	- 22 - 19	- 20	330 319	324	352 338	345
Zinc . .	- 117 - 120	- 118	264 259	261	381 379	380
Cadmium . .	- 592 - 587	- 589	292 288	290	884 875	879

justify conclusions being drawn as to their relative merits under these conditions. All the comparison materials showed considerably more attack. Assigning the figure 100 to the average weight of metal attacked in the case of the tin specimens, the corresponding relative figures for the other materials are: Nickel 271, Copper 288, Brass 305, Zinc 336 and Cadmium 778.

V. Tensile Tests.

The effect of atmospheric exposure on the mechanical strength of the 3 varieties of tin and for comparison on cadmium and copper, was investigated in the following way. The specimens employed were 6 inch lengths of 18 S.W.G. wire and during exposure they were clamped to wooden frames, provision being made for removing half the number of specimens of each material after any required period of exposure. Twenty-four specimens of each material were exposed and a similar number of "blanks" were stored in desiccators in the laboratory. To avoid, as far as possible, discrepancies arising from variations in gauge, specimens for exposure and "blanks" of the same material were cut from the same coil of wire, thoroughly mixed and the specimens for exposure selected at random.

After 10 months, half the number of specimens of each material were removed, and their breaking loads compared with some of the unexposed specimens. The remainder were tested in a similar manner after a further 10 months' exposure.

The breaking load measurements were made on a small wire testing machine, and in the case of the tin and cadmium specimens, in view of their small breaking loads and the importance of the time factor, a special method of testing was evolved. This consisted in determining the time taken for

breaking on five or six different loads. Curves were then drawn, plotting loads as abscissae. It was found that in every case these curves were hyperbolic functions, since by plotting the logarithms of load against the logarithms of time, straight lines were obtained. The relationship between load and time is thus of the form: $\log W = n \log t + K$ where W is the load (in lb.), t the time (in mins.) taken to break at this load, n the slope of the line and K a constant.

The value of n was obtained from the graph and by substituting this in the above equation, together with values of $\log W$ and $\log t$, the constant K was obtained. But in the limiting case where t approaches zero, $\log W = K$, or $W = \text{antilog } K$. By this means, accurate comparative values were obtained for the breaking loads.

In addition, the elongation of each specimen was measured and the effect of exposure on the ductility of the materials was thus obtained.

With regard to the copper specimens, the procedure adopted consisted of applying a load of 60 lb. gradually during the first five minutes, and then continuing with a uniform rate of loading of 1 lb. per minute.

A summary of the results of these determinations is given in Table V., and the relationships obtained between breaking load and time of breaking in the case of the tin specimens are plotted in Fig. 6.

TABLE V.—SUMMARY OF TENSILE TESTS.
(LENGTH OF TEST SPECIMENS = $3\frac{1}{2}$ INS.)

Material.	Initial Measurements of Blanks.		Measurements after 10 Months.				Reductions due to Corrosion in 10 Months.				Measurements after 20 Months.				Reductions due to Corrosion in 20 Months.			
			Blanks.		Exposed Specimens.						Blanks.		Exposed Specimens.					
	Breaking Load (lb.).	Elongation (%).	Breaking Load (lb.).	Elongation (%).	Breaking Load (lb.).	Elongation (%).	Reduction in B.L. (lb.).	Percentage Reduction in B.L. (lb.).	Reduction in Elongation (%).	Percentage Reduction in Elongation.	Breaking Load (lb.).	Elongation (%).	Breaking Load (lb.).	Elongation (%).	Reduction in B.L. (lb.).	Percentage Reduction in B.L. (lb.).	Reduction in Elongation (%).	Percentage Reduction in Elongation.
Pure Tin . .	7.37	52	7.29	52	6.86	44	0.43	5.8	8	15	7.14	50	6.64	44	0.50	6.8	6	12
Antimonial Tin (Pure Tin + 2.2 % Antimony) .	11.82	48	11.65	48	11.14	45	0.51	4.3	3	7	11.53	50	10.62	41	0.91	7.7	9	19
Cupriferosus Tin (Pure Tin + 0.2 % Copper) .	8.61	67	8.60	67	8.39	53	0.21	2.4	14	21	8.56	67	8.13	50	0.43	5.0	17	25
Cadmium . .	18.3	82	18.9	82	16.9	67	2.0	7.6	13	16	19.2	80	15.9	59	3.3	18.0	21	26
H.C. Copper	66.5	49	66.5	49	65.2	44	1.3	2.0	5	10	66.5	49	63.6	40	2.9	4.4	9	18

It will be noticed from this table that whereas the tin alloys showed a fairly uniform rate of attack throughout the two periods of exposure, the pure tin was badly affected in the first 10 months but showed relatively little change as a result of the second 10 months' exposure.

The second interesting feature is the behaviour of the tin containing copper. During the first 10 months this material suffered 21 per cent. reduction in elongation, although its breaking load was the least affected of the 3 materials. The next 10 months, however, only resulted in reducing its elongation by a further 4 per cent.

In comparison with the other materials tin proved slightly inferior to copper but superior to cadmium. After the first 10 months, the average percentage reduction in breaking load of the tin specimens was 4.2 per cent.,

whilst copper showed 2.0 per cent. and cadmium 7.6 per cent. respectively. After the 20 months' exposure the corresponding figures were: tin 6.5 per cent., copper 4.4 per cent. and cadmium 18.0 per cent. The reduction in elongation figures after 10 months were: tin 14 per cent., copper 10 per cent. and cadmium 16 per cent. and after 20 months: tin 19 per cent., copper 18 per cent. and cadmium 26 per cent.

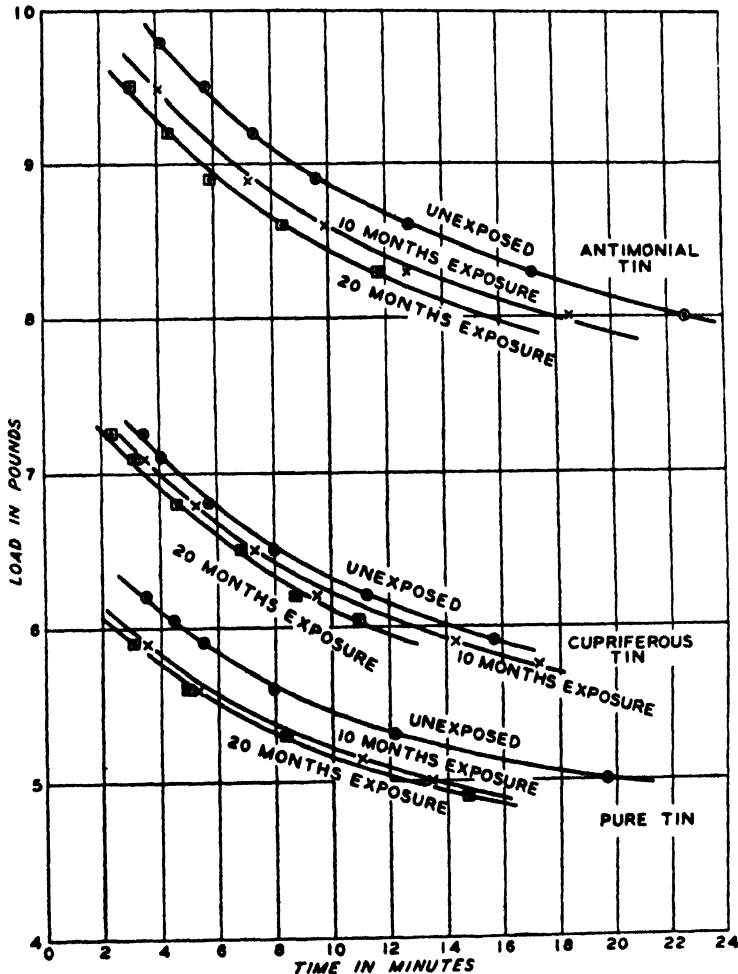


FIG. 6.—Tensile tests on tin wires. Relation between breaking load and time of breaking, for unexposed specimens and for specimens after 10 months and 20 months complete exposure outdoors.

VI. General Conclusions.

(1) Samples of pure tin and of pure tin alloyed with antimony and with copper have been exposed, with samples of copper, brass, nickel, zinc and cadmium for comparison, to the following three types of atmospheres: Indoors, outdoors shielded from rain and outdoors unshielded. Although showing considerable variation among themselves, all the materials tested suffered relatively little attack. For example, under

conditions of complete exposure outdoors, the penetration of the material which suffered the greatest attack, calculated from the weight of metal corroded per unit area, was only 0.0004 inch per year.

(2) In indoor atmospheres, in the absence of chemical fumes, pure tin and pure tin alloyed with 2.2 per cent. antimony and with 0.2 per cent. copper are attacked less than copper, zinc or cadmium. Under these conditions pure tin shows a slight but definite superiority over the alloyed tins.

(3) The relationship between the weight increment and the time of exposure for tin, in an indoor atmosphere, is a linear function except for the first three or four days' exposure. The film formed is probably therefore of a granular nature and not of the continuous protective type.

(4) Under conditions of exposure to a vigorous current of air and to diurnal fluctuations of temperature and humidity, but sheltered from direct rainfall (*i.e.*, as in the Stevenson screen), pure tin and pure tin alloyed with 2.2 per cent. antimony and with 0.2 per cent. copper proved superior to nickel in their resistance to attack, but slightly inferior to copper. The Stevenson screen method was insufficiently sensitive, however, to differentiate between the pure tin and the two tin alloys.

The rate of corrosion under Stevenson screen conditions is closely associated with the deliquescent nature of the corrosion products. Consequently nickel, which forms a very deliquescent corrosion product, suffered more than copper under these conditions, whereas under conditions of complete outdoor exposure, nickel proved more resistant than copper.

(5) Under conditions of complete exposure outdoors, pure tin and pure tin alloyed with 2.2 per cent. antimony and with 0.2 per cent. copper showed no marked differences in their resistance to attack. All the tin specimens were superior to the comparison materials tested, which showed increasing rates of attack in the following order: nickel (least attack), copper, brass, zinc and cadmium (most attack).

(6) The effect of complete outdoor exposure on the mechanical properties of the pure tin and the two tin alloys was somewhat variable. The average value of the three materials would appear to indicate, however, that tin is affected slightly more than copper but less than cadmium.

Summary.

A study has been made of the behaviour of pure tin and pure tin alloyed with 2.2 per cent. antimony and with 0.2 per cent. copper, when exposed to the following three types of atmosphere: Indoor, outdoor shielded from rain and outdoor unshielded. A few samples of copper, 70/30 brass, nickel, zinc and cadmium were also exposed for comparison. The effects of exposure were measured by (a) weight increment tests on plates exposed indoors and on coils of wire exposed in a Stevenson screen (outdoor atmosphere shielded from rain), (b) loss in weight tests on plates exposed outdoors, and (c) tensile tests on wires exposed outdoors.

Apart from the indoor atmosphere, where pure tin proved slightly more resistant to attack than the two tin alloys, the addition of 2.2 per cent. antimony and 0.2 per cent. copper to pure tin has little effect on its resistance to atmospheric corrosion. The weight increment/time curve for tin and the two tin alloys indoors was rectilinear after the first few days' exposure, the film formed being of a non-protective type.

With two exceptions the tin and tin alloys were corroded less than the

comparison materials, copper proving slightly superior under Stevenson screen conditions and also as regards mechanical properties when exposed outdoors.

This investigation was carried out for the British Non-Ferrous Metals Research Association with the support of the Tin Research and Industrial Applications Committee. For permission to publish the present paper, the author is indebted to the Director and Council of the British Non-Ferrous Metals Research Association and to the International Tin Research and Development Council.

His best thanks are due to Professor R. S. Hutton and Dr. O. F. Hudson for their valued advice and to Dr. J. C. Hudson for his encouragement and guidance during the early stages of the work.

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THE DIPOLE MOMENTS OF ISOTOPIC MOLECULES.

By R. P. BELL.

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The equilibrium interatomic distances in a molecule are practically unaltered by the substitution of one isotope for another, and it would therefore be anticipated on the basis of a static model that the dipole moment will also be unchanged. Actually, however, any molecule in its lowest state possesses a half quantum of vibrational energy, the amplitude of which will depend on the mass of the atoms. The present paper gives an investigation of the problem on this basis.

Let the equilibrium distance between the atoms of a diatomic molecule be a and the amplitude of vibration about this position be b . Then if the motion is assumed to be simple harmonic (as is very nearly true for the lowest vibrational state) the interatomic distance x can be written

$$x = a + b \sin \omega t$$

where t is the time. The instantaneous dipole moment μ will be some function of x , $\phi(x)$, and the observed dipole moment $\bar{\mu}$ will be given by the time average of μ over a whole vibration, *i.e.*,

$$2\bar{\mu} = \frac{\int_0^{\pi} \phi(a + b \sin \theta) d\theta + \int_0^{\pi} \phi(a - b \sin \theta) d\theta}{\int_0^{\pi} d\theta}$$

$$\bar{\mu} = \frac{1}{\pi} \int_0^{\pi} \{\phi(a + b \sin \theta) + \phi(a - b \sin \theta)\} d\theta \quad . \quad . \quad (1)$$

where $\theta = \omega t$.

The form of $\phi(x)$ depends on the nuclear charges and the electronic distribution in the molecule, and should in principle be deducible from

quantum-mechanical principles. However, such calculations are not in general available, and we shall therefore write $\phi(x)$ in the form

$$\mu = \phi(x) = \sum_n A_n x^n \quad . \quad . \quad . \quad (2)$$

where n may have both positive and negative values. Equation (1) then becomes

$$\bar{\mu} = \frac{1}{\pi} \int_0^{\pi} \sum_n A_n \{ (a + b \sin \theta)^n + (a - b \sin \theta)^n \} d\theta \quad . \quad (3)$$

It is clear that $\bar{\mu}$ will not in general be equal to the equilibrium value $\mu_0 = \sum_n A_n a^n$: in fact this will only be so if n is restricted to the values

0 and 1. In this case $\mu = \mu_0 + A_1 x$, which corresponds to a dipole consisting of two non-polarisable charges. Any actual molecule constitutes a polarisable system, so that in practice we may expect $\bar{\mu}$ to depend on the amplitude b and hence on the masses of the particles.

If the power series (2) is known, each term of (3) can be integrated by expanding in powers of $\sin \theta$. The simplest case is that of a dipole consisting of two ions of charges $+e$ and $-e$ (where e is of the order of magnitude of the electronic charge), one of which is non-polarisable (*i.e.*, an atomic nucleus), while the other has a polarisability α . We then have

$$\mu = ex - \frac{e\alpha}{x^2}, \quad \mu_0 = ea - \frac{e\alpha}{a^2},$$

and equation (3) becomes

$$\begin{aligned} \bar{\mu} &= ea - \frac{e\alpha}{\pi} \int_0^{\pi} \left\{ \frac{1}{(a + b \sin \theta)^2} + \frac{1}{(a - b \sin \theta)^2} \right\} d\theta \quad . \quad (4) \\ &= \mu_0 - \frac{e\alpha}{a^2} \left\{ \frac{1 \cdot 3}{2} \left(\frac{b}{a} \right)^2 + \frac{1 \cdot 3 \cdot 5}{2 \cdot 4} \left(\frac{b}{a} \right)^4 + \dots \right\}. \end{aligned}$$

Since $\frac{b}{a} < \frac{1}{10}$, it is sufficient to retain only the first term of the expansion.

The difference between $\bar{\mu}$ and μ_0 is small, and is without interest for a single molecule at ordinary temperatures. It is, however, of interest when dealing with isotopes: thus if we are comparing two molecules containing respectively isotopes of masses m_1 and m_2 , we have

$$b_1/b_2 = \sqrt[4]{m_2/m_1},$$

and hence

$$\mu_2 - \bar{\mu}_1 = \frac{3e\alpha b_1^2}{2a^4} \left(1 - \sqrt{\frac{m_1}{m_2}} \right). \quad . \quad . \quad . \quad (5)$$

The differences predicted by this equation are outside the range of present experimental accuracy for most pairs of isotopes, but for hydrogen and deuterium the value of $\mu_D - \bar{\mu}_H$ should be of the order of

$$0.01 - 0.05 \times 10^{-18} \text{ e.s.u.}$$

This figure is very uncertain, owing to the crude nature of the model employed, but it indicates that such differences are worth looking for experimentally. A difference of this kind may be a partial explanation

of the results of Bell and Wolfenden,¹ who found that in dioxan solution the D₂O molecule exhibits a greater osmotic abnormality than the H₂O molecule.

Summary.

(1) The observed dipole moment of a molecule will in general be a function of its amplitude of vibration, except in the case of a dipole composed of non-polarisable charges.

(2) There will in consequence be a difference in the dipole moments of isotopic molecules. Calculation on the basis of a simple model indicates that this difference may be detectable experimentally in the case of compounds of hydrogen and deuterium.

Since the above note was written, J. M. A. de Bruyne and C. P. Smyth² have reported that the dipole moment of ND₃ exceeds that of NH₃ by 0.03×10^{-18} e.s.u. This type of molecule presents a more complex problem than the simple diatomic case treated above, partly because there are several possible modes of vibration, and partly because the equilibrium angle between the bonds depends on the mass of the atoms. De Bruyne and Smyth state that the observed dipole moment will not depend on the mass of the nuclei for strictly harmonic vibrations: as shown above this is only true if the changes in electron distribution can be neglected. For anharmonic vibrations there will in general be a difference between $\bar{\mu}$ and μ_0 even for non-polarisable charges.

¹ *J. Chem. Soc.*, 1935, 822.

² *J. Amer. Chem. Soc.*, 1935, **57**, 1203.

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ON THE RELATION BETWEEN PARTICLE SIZE AND CATAPHORETIC MOBILITY.

BY IAN KEMP.

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The object of this paper is to review the theory of cataphoresis, and to give an account of some experiments intended to test the validity of the equations.

The original cataphoresis equation of Helmholtz¹ has been modified by Lamb² and by Smoluchowski,³ who in 1903 derived the Helmholtz equation for the cataphoresis of a rigid non-conducting particle suspended in a viscous medium and surrounded by an ionic double layer of the Helmholtz type.*

The equation deduced was that obtained by Helmholtz¹:

$$V = \frac{DX\zeta}{4\pi\eta}, \quad \dots \quad (1)$$

* An excellent review of the theoretical developments is given by Mueller.^{1a}

where V is the velocity of cataphoresis, D the dielectric constant, the coefficient of viscosity, X the intensity of the electric field, and ζ is the potential difference across the double layer.

After their development ^{4, 5} of the theory of strong electrolyte solutions, Debye and Hückel applied their theory to the theory of cataphoresis ^{6, 7} and deduced the following expression for the velocity of cataphoresis :

$$V = C \frac{DX\zeta}{\eta}, \quad . \quad . \quad . \quad . \quad (2)$$

where C is now a constant dependent upon the shape of the particle, being equal to $\frac{1}{3}\pi$ for a sphere, and $\frac{1}{2}\pi$ for a cylinder whose axis is parallel to the field. Thus for a sphere

$$V = \frac{DX\zeta}{6\pi\eta}$$

which is the Stokesian form of the equation.

According to the theory of Debye and Hückel ^{4, 5} the electro-kinetic potential for a sphere is given by the expression

$$\zeta = \frac{E}{Db(1 + \kappa b)}, \quad . \quad . \quad . \quad . \quad (3)$$

where E is the charge, b the radius, and κ is defined by the equation

$$\kappa = \sqrt{\frac{4\pi e^2}{DkT} \sum n_i \nu_i^2},$$

where e is the electronic charge, k the Boltzmann constant, T the absolute temperature, and n_i is the number of ions of valency ν_i per c.c. of solution. Thus

$$\kappa = \sqrt{\frac{4\pi e^2}{DkT} \frac{2N}{1000} \mu} = 3.28 \cdot 10^7 \sqrt{\mu} \text{ at } 20^\circ \text{ C},$$

where μ is the ionic strength.

The quantity κ has the dimensions of a reciprocal length, and is identified by Debye and Hückel with the reciprocal of the thickness of the ionic atmosphere. The final equation (2) of Debye and Hückel thus differs from that of Smoluchowski by a numerical factor.

The discrepancy between the two equations was finally resolved in 1931 by Henry, ⁸ who showed that the difference was due to the fact that Debye and Hückel had not considered the distortion of the electric field by the particle, whose conductivity they had in fact taken to be equal to that of the liquid.

Henry discusses the general case of a particle of specific conductivity μ suspended in a liquid of specific conductivity μ' , and by using the postulates and analytical methods of Debye and Hückel, he arrives at the following expression for the velocity of an insulating particle ($\mu' \gg \mu$):

$$V = \frac{DX\zeta}{4\pi\eta} f(\kappa b), \quad . \quad . \quad . \quad . \quad (4)$$

where the value of $f(\kappa b)$ can be calculated more or less accurately over the whole range of κb . The function $f(\kappa b)$ is plotted as curve 1, of Fig. 1, which is taken from Henry's paper.

It is clear that the Smoluchowski expression holds only when $\kappa b > 300$, whilst the Debye-Hückel equation is valid when $\kappa b < \frac{1}{2}$. The Debye-Hückel equation is correct only for small values of κb , *i.e.* where the particle is small compared with the thickness of the ionic layer, in which case the distortion due to an insulating particle will become negligible.

The equation of Henry is, however, still open to objection on theoretical grounds, as Henry himself has pointed out. Thus it is assumed by Smoluchowski, by Debye and Hückel, and by Henry that the charge distribution inside the ionic atmosphere is unaffected by the external field and by the relative motion of the particle and liquid.

Distortion of the ionic atmosphere during the motion of a particle in a field has been shown by Debye and Hückel to lead to an additional resistance which is termed the "relaxation force." Thus all the derivations previously described have neglected the relaxation force.

Mooney⁹ has attempted to derive an equation for cataphoresis by taking into account the distortion of the spherical symmetry of charge in the ionic atmosphere due to the relative motion of particle and liquid in an electric field. He does not publish his derivation, but states that a complete solution of his equations could not be obtained.

The mechanism of the process of cataphoresis has been very clearly described by Paine¹⁰ who has recalculated the Debye-Hückel expression of cataphoresis, taking into account the relaxation force. He obtains the equation

$$V = \frac{XE}{6\pi\eta b} \left[1 - \frac{k}{1+k} - \frac{a}{b} \frac{E^2 \kappa}{6DkT(1+k)} \right], \quad (8)$$

where a is the radius of the ions in the ionic atmosphere, and the other symbols are as before. In this equation, the first term is the Stokesian term, the second is the "electrophoretic term," which corrects for the thickness of the double layer and finite size of the particle, while the third gives the effect of the "relaxation force."

Paine points out that for an ion the last two terms are of comparable magnitude, and the relaxation force cannot therefore be neglected.

Gilford¹¹ has suggested that the appreciable mobility exhibited by conducting particles may be due to the existence of the relaxation force. On the other hand, Henry suggests that the effect may possibly be attributed to the effect of surface polarisation. Bull¹² suggests that the results of Bull and Söllner¹³ with nonpolarisable mercury particles in mercurous nitrate solution are in disagreement with this explanation of Henry. The equation of Paine is unfortunately based upon the equations of Debye and Hückel, which, as we have seen, are concerned only with particles whose conductivity is equal to that of the liquid.

The magnitude of the relaxation term in Paine's equation depends upon the charge and size of the particle.

Thus for the single ions, the relaxation term is of reasonable dimensions, but for colloidal particles of quite small surface charge density, the term

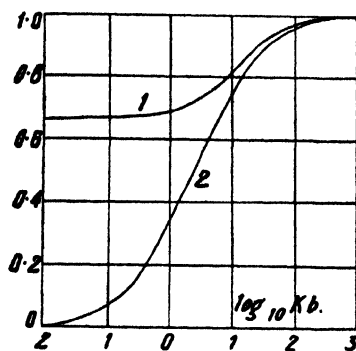


FIG. 1.

becomes too large, indicating some serious error in the equations of Paine.

Mueller¹² has also pointed out that the equations so far published neglect the known variation of conductivity at the surface and also the polarisation of the surface charge. Furthermore, it is not certain how the electrical forces on the ions are transferred to the liquid itself.

If the effect of the electric field in polarising the charge in the double layer and at the surface of the particle is of importance, then the mobility of a particle (*i.e.*, its velocity under unit applied field) should vary with the intensity of the field, and furthermore, the effect should become more marked on diluting the solution which surrounds the particle. No such variation has been observed by other workers, and some experiments made by the author have shown no appreciable alteration in the mobility of a particle with varying field strength. These experiments were made with gliadin-covered quartz particles, and with silica particles in dilute solutions of ionic strengths 10^{-4} and 10^{-5} , the range of field intensities being from 3 to 15 volts/cm. No definite variation could be detected. Such an effect as we have outlined, if existent, would therefore seem to be within the experimental error, *i.e.*, \pm ca. 5 per cent.

The various equations of cataphoresis give the relation between the velocity of cataphoresis, the electrolyte concentration, and the size of the particle. The velocity is thus a function of two variables if the surface charge density be constant, and the theoretical relation can be tested by varying either of these variables. In actual fact, it is very difficult to find a colloid particle whose surface charge density does not vary with the electrolyte concentration. Thus the verification of the theoretical equations by observations of the variation of mobility with electrolyte concentration is unsatisfactory. For example, the results of Audubert¹³ are impossible to interpret, since there is no certainty that the surface charge density σ of the particles which he used remained constant on varying the ionic strength. Again, even with protein-covered particles in solutions of constant p_H , the value of σ appears to vary in very dilute solutions (Kemp and Rideal¹⁴).

It is clear that more reliable results may be expected from measurements of the variation of velocity with the particle size in solutions of constant electrolyte concentration, since here we may assume σ to remain constant, as there appears to be no reason for supposing that it will vary with the size of the particle, especially if the variation in the latter is small.*

The relations between the cataphoretic velocity and the particle size predicted by the various theoretical equations are as follows:

(1) Debye and Hückel:

$$V = \frac{2X\sigma}{3\eta} \frac{b}{1 + \kappa b} \quad . \quad . \quad . \quad (10)$$

(2) Paine:

$$V = \frac{2X\sigma}{3\eta} \frac{b}{1 + \kappa b} \left[1 - \frac{8\pi^2 a \sigma^2}{3DkT} b^3 \kappa \right] \quad . \quad . \quad . \quad (11)$$

(3) Henry:

$$V = \frac{X\sigma}{\eta} \frac{b}{1 + \kappa b} f(\kappa b) = \frac{X\sigma}{\eta \kappa} \frac{\kappa b}{1 + \kappa b} f(\kappa b) \quad . \quad . \quad (12)$$

The function $\frac{\kappa b}{1 + \kappa b} f(\kappa b)$ is plotted as curve 2 of Fig. 1.

* This effect has been discussed by Abramson²² and by White, *etc.*²⁷ See also the paper of Koch.²⁸

From a theoretical point of view, the equation of Henry is the most satisfactory of the three, for reasons which we have previously given.

Quite a considerable number of investigations have been made of the relation between particle size and cataphoretic mobility. The experimental evidence has been reviewed by Abramson²³ and by White, Monaghan and Urban.²⁷

In 1903 Hardy¹⁵ found that the mobilities of protein sols in acetic acid showed no variation with size. Similar conclusions were reached by Burton¹⁶ for silver sols, and by McTaggart¹⁷ for gas bubbles of diameter 60-160 μ in water and in dilute electrolytes. The results of Mooney¹⁸ were in disagreement with those of previous workers in this field. He found for droplets of various oils suspended in water and in dilute solutions, a decrease of mobility with particle size. His results are only in rough agreement with the predictions of equations (10) and (12).

Further and more detailed experiments were made by Abramson and his co-workers^{19, 20, 21, 22} with different types of particles, both solid and liquid, whose size varied from 0.5 to 50 μ . Various electrolyte solutions were used.

Abramson concludes that in general the mobility of a particle is independent of its size.

Many of the previous experiments¹⁵⁻²² were made with quite large particles in relatively strong solutions, *i.e.*, in a region where, according to Henry, no variation in the mobility could be expected. With regard to the case of Mooney's oil-drop experiments, it must be pointed out that observations made with fluid droplets form an unsatisfactory basis for testing a theoretical expression which was originally derived for rigid particles. Thus, Henry finds that the cataphoretic velocity of liquid drops is considerably affected by a circulatory motion inside the drop. In addition, appreciable distortion of the charged droplet may occur in the electric field.

The object of the experiments described in this paper was to investigate small insulating particles in dilute electrolytes, *i.e.*, in a region where a variation of mobility with particle size should manifest itself.

Experimental.

1. Preparation of Uniform Suspensions.

Suspensions of particles of gamboge and of silica were employed in these experiments. The gamboge suspensions were prepared by shaking the solid with distilled water, and similarly, in the case of silica suspensions, ground-up silica gel was shaken with water. The particles obtained were roughly spherical, judging from their ultramicroscopic appearance and their behaviour in flow. Both substances have a very low specific conductivity. Uniform suspensions were prepared by the method of fractional sedimentation in the centrifuge, which incidentally served to eliminate traces of electrolytes, thus obviating the necessity for dialysis.

2. Determination of Particle Size.

(a) **Direct Measurement.**—Using a magnification of 1000 in conjunction with any eyepiece scale, it was possible to measure particles with an accuracy of $\pm 0.5\mu$ for particles of radius greater than 0.5μ .

(b) **Counting and Analysis.**—The particles were counted in a slit ultramicroscope with a beam of known thickness, using an eyepiece graticule. The mass of solid was estimated by evaporation of a known volume

of the suspension. The densities of the materials were measured by a density bottle method.

If m be the mass of solid of density ρ in a volume of suspension v containing n spherical particles per unit volume, then the radius b is given by the expression

$$b = \left(\frac{3m}{4\pi\rho v n} \right)^{\frac{1}{3}} \quad (13)$$

The accuracy of the method is limited by the quantities ρ and n . If the particle be solvated then the effective radius will be larger than that calculated from equation (13). For a particle of radius 10^{-5} cm. the error in the estimated radius arising from solvation is only 3 per cent., assuming we have a hydration layer of even five molecular thicknesses. The accuracy with which n could be estimated was about ± 8 per cent., the error being somewhat less in the case of silica particles owing to their different refractive index.

The results obtained by this method with particles of radius greater than 0.5μ were found to be in agreement with direct measurement, the difference being about ± 6 per cent. for large particles.

3. Experimental Investigation of the Relation between Size and Mobility.

The cataphoretic velocities of the particles were measured by means of a microcataphoresis apparatus of the cylindrical tube type in conjunction

with a Leitz slit-ultramicroscope, the apparatus being kept in an air thermostat at $20^{\circ}\text{C.} \pm 0.2^{\circ}$.

The ranges of particle radii were, in the case of gamboge, from 0.1μ to 0.5μ , and for silica 0.2μ to 1.0μ , the particles being suspended in potassium chloride solutions whose ionic strength varied from 10^{-2} to 10^{-4} . The value of the ionic strength was known with an accuracy of better than ± 1 per cent. except for solution of $10^{-2} N$, where contamination by carbon dioxide from the atmosphere and by electrolytes from the glass vessels may alter the ionic strength. In order

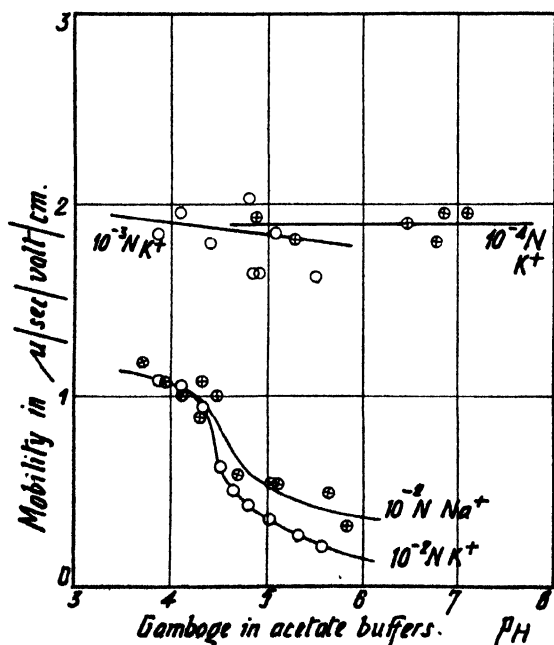


FIG. 2.—Gamboge in alkali acetate buffers.

to minimise this error, CO_2 -free water and fresh solutions were used. Interaction between the colloidal particles could be neglected since the average concentration was only 10^8 particles per c.c.

In the case of colloidal particles whose surface charge is determined by surface ionisation, such as colloidal acids, bases, and ampholytes, small changes in the hydrogen ion activity of the solution may result in appreciable

variation in value of σ . It was therefore of importance to investigate first the relation between the p_H of the solution and the surface charge density for the colloids employed in these experiments. This was done by measuring the cataphoretic velocities of particles of constant size in solutions of varying p_H . The buffer solutions used were mixtures of sodium and potassium acetates and acetic acid, the p_H values being determined by the quinhydrone electrode and by the glass electrode. The results are shown in Figs. 2 and 3.

The mobilities of particles of both gamboge and of silica show very little change with p_H of the solution. The variation which is shown by gamboge in $10^{-3} N$ solutions of alkali-acetate and acetic acid is due to variations in the concentrations of the strong electrolytes in the buffer solutions, since no attempt was made to keep the ionic strength constant. This reduction in mobility may be due partly to the effect of the decrease in double layer thickness and partly due to the increasing adsorption of alkali metal ions as their concentration in the buffer is increased. It is of interest to note that the adsorption of potassium ions is greater than that of the sodium ions at a similar concentration. For more dilute solutions, where the adsorption of buffer ions is considerably less, no variation of mobility with p_H is observed.

In the case of silica particles in $10^{-3} N$ buffer, the ionic strength was

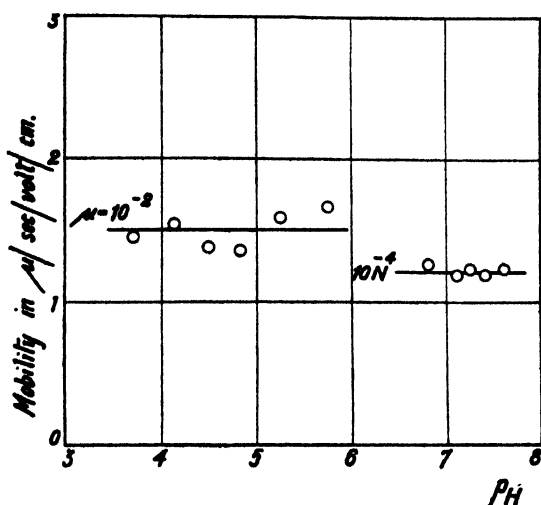


FIG. 3.—Silica in potassium acetate buffers.

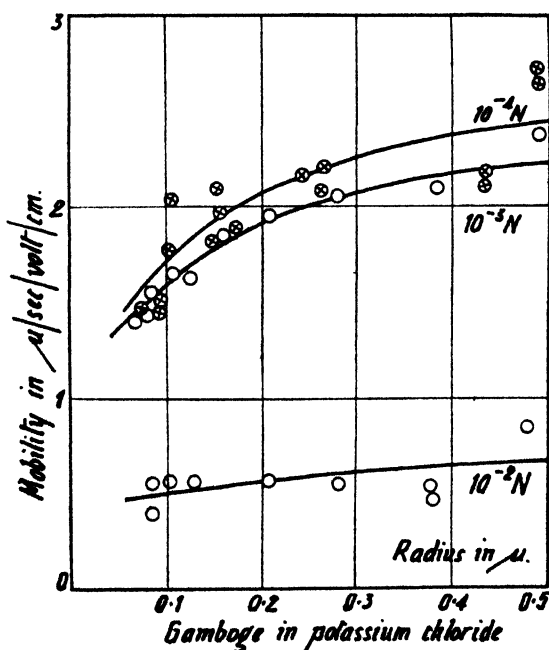


FIG. 4.

kept constant at 10^{-3} , and there is no variation in the mobility with p_H at this concentration.

It is clear, then, that small changes in the p_H of the solutions of potassium chloride used in the main experiments will not influence the value of σ for the particles used to an appreciable extent.

Results.

For both suspensions the cataphoretic mobility was found to decrease with decreasing particle size, the slope of the curve relating the mobility to the radius increasing as the electrolyte concentration is decreased, this being in accordance with the theory. The results are shown in Figs. 4 and 5.

The results for gamboge particles in 10^{-5} *N* electrolyte are omitted from Fig. 4 to avoid confusion.

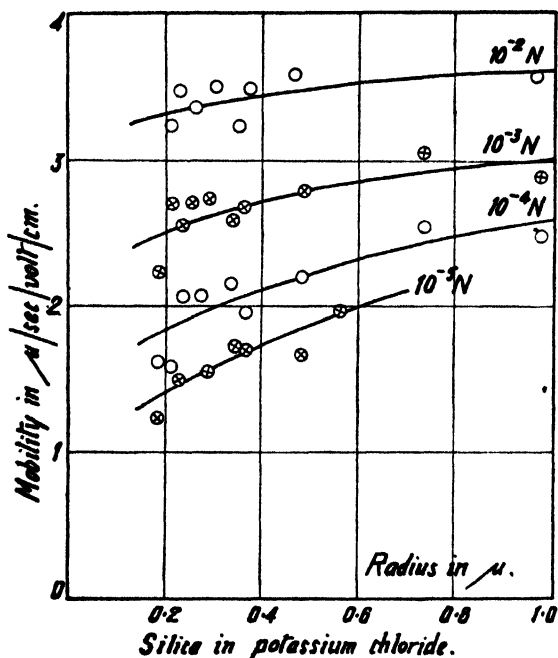


FIG. 5.

concentration, as we have already seen. In the case of gamboge the mobility of a particle of given size decreases on increasing the concentration of salt, whilst silica shows a considerable increase, indicating an appreciable excess adsorption of chloride ions from solution.

There are two methods now of comparing these results with the theory. The curves representing the variation of mobility with radius for each ionic strength are not continuous, since the value of σ varies with the electrolyte concentration. In order to compare the experimental results with the predictions of theory it is convenient to plot the mobility against the quantity $\log_{10} kb$, and this gives us the continuous curves of Figs. 6 and 7, which are derived from the smooth curves of Figs. 3 and 4, the numbers against each curve representing the ionic strengths.

The first method is to compare each individual curve with the theory,

The curves showing the relation between the cataphoretic mobility and the radius can be drawn from the experimental points with an accuracy of 3-4 per cent., except for the low mobilities obtained for gamboge particles in 10^{-3} *N* potassium chloride, where the latitude is about 10 per cent. The uncertainty in the radius is about 6 per cent. at least.

These curves are displaced along the mobility axis, owing to the fact that the surface density of charge is dependent upon the electrolyte

and this is shown in Figs. 6 and 7, where the dotted lines represent the variation of mobility with $\log_{10} \kappa b$ predicted by equation (12).

The agreement between the theory and experiment obtained by this method is shown in the following tables:—

Ionic Strength.	Range κb .	Estimated Accuracy of Experimental Curve.	Mean Deviation between Theory and Experiment.
Gamboge—			
10^{-2}	160-33	10 per cent.	5 per cent.
10^{-3}	52-10	4 "	2 "
10^{-4}	16-3	4 "	1 "
10^{-5}	5-1	3 "	6 "
Silica—			
10^{-2}	330-66	3 "	1 "
10^{-3}	104-21	3.5 "	2.5 "
10^{-4}	33-6	4 "	3 "
10^{-5}	8-2	4 "	2.5 "

The second method of comparison with theory is by correcting for the effect of the variation in σ , and thus obtaining for each substance the complete curve relating the mobility with κb .

Thus assuming the velocity to be proportional to σ , each curve can be multiplied by an appropriate factor, representing a ratio of surface charge densities, in order to obtain the continuous κb

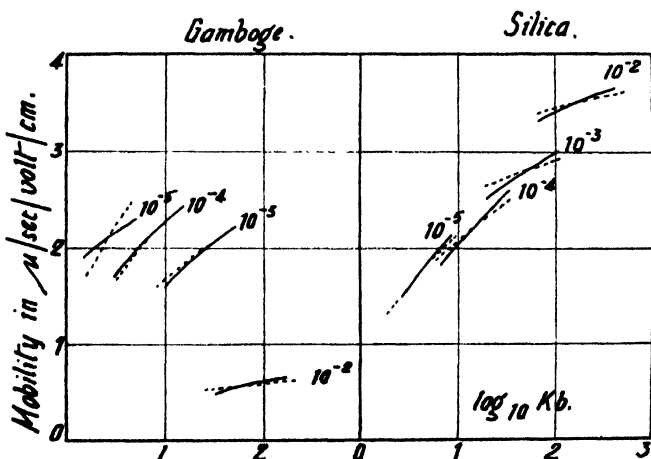


FIG. 6.—Gamboge.

FIG. 7.—Silica.

curve for a constant arbitrary σ value. These composite curves are shown in Figs. 8 and 9, in which the dotted lines represent the predictions of equation (12).

The mean deviations between experiment and theory over the whole curves are 3 per cent. for gamboge and 5 per cent. for silica. The deviations shown in Fig. 8 by gamboge for $10^{-5} N$ electrolyte are probably due to the uncertainty in the ionic strength at such low concentrations.

The two methods of comparison thus agree in showing that the deviation between the experimental results and the predictions of the theory of Henry as embodied in equation (12) are of the same order as the experimental accuracy, *i.e.*, about 5 per cent., for κb values ranging from 2 to 330. The theory of Henry thus applies to the colloidal systems investigated over this range, and it may therefore be relied upon to predict with some accuracy the variation of mobility with particle size.

Although both the types of particle investigated were of low specific conductivity, yet the one, gamboge, represents the hydrophilic type of colloid and the other, silica, is a typical hydrophobic colloid. Thus although this work has of necessity dealt with only two colloids, there is some reason to suppose that the Henry equation will apply equally well to other colloidal systems containing insulating particles.

The importance of the factors which have been neglected in the derivation of the Henry equation would seem to be from these results of the order of 5 per cent. Thus, if an improved version of the theory can be derived, taking into account all the factors which Henry neglected and which have been discussed in the introduction, the experimental accuracy of mobility measurements must be increased.

Although the precision of cataphoretic measurements may be as good as ± 2 per cent. (see Henry²⁴) yet the "reproducibility" of colloidal suspensions is frequently far less than this figure, and this factor, combined with inaccuracies in the determination of the radii of small particles,

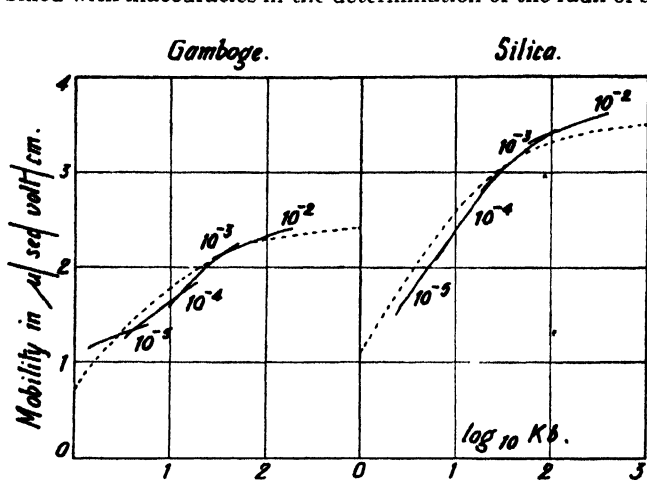


FIG. 8.—Gamboge.

FIG. 9.—Silica.

sets a limit to the precision with which a theoretical relation can be tested experimentally.

The fact that the variation of mobility with particle size is accounted for with some accuracy by the Henry equation

supports the conclusion arrived at in a previous publication,¹⁴ in which it was shown that the variation of the mobility of protein-covered quartz particles with ionic strength could be accounted for by the Henry expression only over the range κb 35-130. Below this range there was considerable discrepancy between theory and experiment, and this was ascribed, not to a breakdown of the theory for small κb values, but to a variation in the value of σ for the protein.

The evidence indicates, then, that the Henry equation is correct to about ± 5 per cent. for insulating particles, and may be relied upon to predict with this accuracy the variation of mobility with size over the range of κb from 2-330, and further to give a satisfactory account of the variation of mobility with ionic strength, providing the surface charge density is constant.

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Summary.

- (1) A review of the present state of the theory of cataphoresis is given.
 (2) The relation between cataphoretic mobility and particle size has been investigated for particles of gamboge and of silica in solutions of potassium chloride of varying concentrations.
 (3) The experimentally determined relation is in agreement with that predicted by the formula of Henry over a range of κb 2-330, the discrepancy being within experimental error (\pm ca. 5 per cent.).

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THE THALLOUS-THALLIC OXIDATION-REDUCTION POTENTIAL.

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The potential of the electrode $\text{Pt} \mid \text{Ti}^{+++}, \text{Ti}^{+}$ is given by the equation :

$$E_1 = E_0 - \frac{RT}{2F} \log_e \frac{a_{\text{Ti}^{+++}}}{a_{\text{Ti}^{+}}}, \quad \dots \quad (1)$$

where $a_{\text{Ti}^{+++}}$, $a_{\text{Ti}^{+}}$ denote the activities of the subscripts; R = gas const./mol; F = 1 faraday; T = temp. abs.; and E_0 = standard potential.

The sign convention is that E_1 shall represent the tendency of +ve electricity to flow spontaneously from electrode to electrolyte.

For the cell $\text{Pt} | \text{Tl}^{+++}, \text{Tl}^+ || \text{H}^+ | \text{Pt}, \text{H}_2, (1 \text{ atm.})$

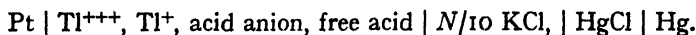
$$E = E_0 - \frac{RT}{2F} \log_e \frac{a_{\text{Tl}^{+++}}}{a_{\text{Tl}^+}} + \frac{RT}{F} \log_e a_{\text{H}^+} \quad (2)$$

if the liquid contact potential is eliminated and the standard hydrogen electrode is defined so that, at any temperature, $E = 0$ for the electrode $\text{Pt}, \text{H}_2 (1 \text{ atm.}), \text{H}^+ (a_{\text{H}^+} = 1)$. To avoid difficulty in the determination of a_{H^+} , it is usual to refer to a solution of HCl in which, instead of a_{H^+} , the mean ion activity, $a_{\pm} = (a_{\text{H}^+} a_{\text{Cl}^-})^{\frac{1}{2}}$, is unity.

E_0 is related to the equilibrium constant $K = a_{\text{Tl}^{+++}}/a_{\text{Tl}^+}$ by the equation :

$$E_0 = \frac{RT}{2F} \log_e K. \quad (3)$$

The thallium oxidation-reduction potential was first investigated by Abegg and Spencer,¹ who measured cells of the type :



The concentration ratio of thalious to thallic ion was varied from ca. 1/5 to ca. 8/1, the total amounts of thallium also varying greatly. All measurements were at 25°, the potential of the $N/10$ calomel electrode being taken as -0.336 volt against the hydrogen electrode standard with the sign convention adopted in the present paper. No corrections were made for the liquid junction potential. For thallium nitrates in nitric acid the values of E_0 at various acidities found by substituting concentrations in an equation of the form of (1), and without allowance for variation of free acid concentration, were as follows :

$[\text{HNO}_3]$ mol/lit.	Average E_0 in volts.
0.42	-1.191 (1.185 to 1.195)
0.413	-1.193
1.0	-1.173 (1.165 to 1.176)
0.3	-1.199

The final value chosen was -1.199 volt for $[\text{HNO}_3] = 0.3$, since it was considered that the liquid junction potential was least in this case. The results for thallium sulphates in sulphuric acid were :—

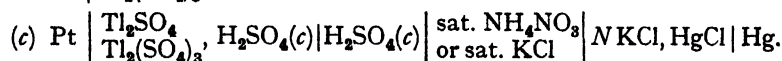
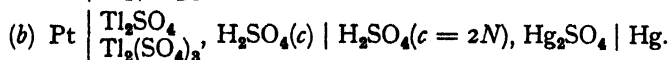
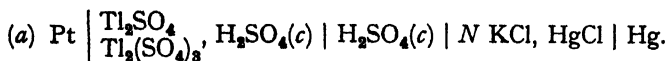
$[\text{H}_2\text{SO}_4]$ mol/lit.	Average E_0 in volts.
0.2259	-1.156 (1.152 to 1.158)
0.09037	-1.163

Abegg and Spencer assumed that the limiting value of E_0 should be the same with both acids, although no measurements could be made in more dilute sulphuric acid, owing to hydrolysis of the thallic salt. Measurements with the chlorides in hydrochloric acid were anomalous, owing to complex-formation. These authors further concluded that, since dilution of a mixture of thalious and thallic salt in a constant concentration ratio had little or no effect on the E.M.F. in the case of the nitrates and sulphates, the ionic concentration ratio $[\text{Tl}^{+++}]/[\text{Tl}^+]$ was constant, and thus either both thalious and thallic salt were almost completely ionised at all concentrations, or (less probably) their relative degree of dissociation was unaffected by dilution. The value -0.3334

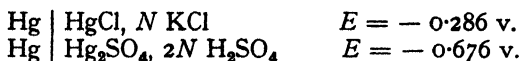
¹ *Z. anorg. Chem.*, 1905, 44, 379.

volt for the potential of the decinormal calomel electrode * would alter the standard potential found by Abegg and Spencer from -1.199 to -1.196 volt, but this is referred to a salt concentration, not ion activity, ratio of unity.

The oxidation-reduction potential was then studied by Grube and Hermann,³ who used cells of the types:—



The values assumed for the reference electrodes on the hydrogen electrode standard were:



at 18° , the temperature at which the cells were measured ($18 \pm 0.5^\circ$). In cell (b), when the concentration c of free sulphuric acid in the Ti electrode compartment was about $2N$, and the free acid concentration was thus almost the same throughout the cell, there would be no appreciable liquid junction potential, and it was assumed that in this case the E.M.F. measurements were most accurate. The values of the E.M.F. obtained with cell (c) were the same (referred to the hydrogen electrode) as for cell (b), and since the calomel electrode was more convenient, most of the measurements were made with cell (c), it being assumed that the salt-bridge completely eliminated the liquid junction potential, which, by comparing cells (a) and (c), was found to be 0.0295 volt for c ($[\text{H}_2\text{SO}_4]$ in Ti compartment) = $1.964 N$.

Grube and Hermann confirmed the observation of Abegg and Spencer that the standard oxidation-reduction potential was independent within wide limits (i) of the concentration ratio $[\text{Ti}^{+++}]/[\text{Ti}^+]$ (which was used instead of the activity ratio in evaluating E_0 by equation 1), (ii) of the total thallium content of the solution, and (iii) of the free acid concentration, provided that the last was sufficient to prevent hydrolysis of thallic salt. The values of E_0 in various free acid concentrations were found to be:

$[\text{H}_2\text{SO}_4]$ mol/lit.	E_0 volts (average).
0.982	-1.2113 (1.2108 to 1.2119)
0.2095	-1.2115 (1.2113 to 1.2118)
0.1047	-1.2117
0.0527	-1.2152
0.0262	-1.1941
0.0131	-1.1769

The value of E_0 adopted was -1.211 volt at 18°C . The data for the potential and temperature coefficient of the normal calomel electrode given by Glasstone,⁴ lead to the value for the potential at 18° , referred to the hydrogen electrode standard, of -0.2809 (corrected) plus

* *Int. Crit. Tables*, 1929, vi., 332.

³ *Z. Elektrochem.*, 1920, 26, 291.

⁴ "The Electrochemistry of Solutions," 1930, p. 292.

tion (4) in the case of zero thallium content may be written (f = activity coefficient, and c = gram-ion concentration) in the form :

$$E' - \frac{RT}{F} \log_e a_{H^+} + \frac{RT}{2F} \log_e \frac{c_{Tl^{+++}}}{c_{Tl^+}} = E_0 - \frac{RT}{2F} \log_e \frac{f_{Tl^{+++}}}{f_{Tl^+}}, \quad (5)$$

which shows that extrapolation of the quantity $(E' - \frac{RT}{F} \log_e a_{H^+})$, the E.M.F. of the cell with zero thallium content referred to the standard hydrogen electrode ($a_{H^+} = 1$), against $[H_2SO_4]$ to $[H_2SO_4] = 0$, gives the value of E_0 , since the thallium ion activity coefficients are both unity at zero ionic strength, and the ratio of thallium ion concentrations is either practically unity, or if not quite unity, the necessary small correction can readily be calculated from (5).

This method of finding E_0 seems to be free from difficulties connected with liquid contact potentials. Such a difficulty arises, however, in the determination of a_{H^+} for H_2SO_4 at various concentrations. However, it is possible to obtain the required a_{H^+} values, as will be explained in the discussion.

Experimental.

(a) Preparation, Purification and Analysis of Materials.

Thallous sulphate was prepared by dissolving pure thallous carbonate in a slight excess of dilute sulphuric acid (A.R. quality in conductivity water), recrystallising the thallous sulphate six times from conductivity water and drying at $130^\circ C$. Analysis (ppt. TII) agreed with theory.

Thallous sulphate dissolved in aqueous A.R. sulphuric acid was oxidised anodically to thallic sulphate by the method of Grube and Hermann²; cathode and anode compartments were separated by a sintered glass septum to avoid cathodic reduction of thallous sulphate to thallium metal.

The resulting solution was mixed with a solution of thallous sulphate such that $[Tl^+] = [Tl^{+++}]$ approximately, and the composition of this stock solution determined as follows:—

$[Tl^{+++}]$ was determined by adding excess potassium iodide to a known volume of the solution, giving a ppt. containing TII and TlI_3 . The latter, equivalent to the thallic sulphate originally present, was rapidly titrated with thiosulphate, the end-point after adding starch being indicated by the colour-change of the ppt. from green (yellow TII + brown TlI_3 + starch iodide), to bright yellow (TII), the last few drops of thiosulphate being added slowly with vigorous shaking. An accuracy of about 0.1 per cent. was obtained. The thiosulphate solution was made up in $m/100$ sodium borate to prevent decomposition by atmospheric carbon dioxide³ and was standardised iodometrically against A.R. potassium permanganate.

The total thallium was determined by reducing completely to thallous sulphate with sulphur dioxide, gently boiling off excess of the latter, neutralising free acid with ammonia and precipitating with potassium iodide.

The total SO_4 radical was estimated as $BaSO_4$ after previous removal of all Tl^+ by precipitation with excess hydrochloric acid.

The mixed solution of thallium sulphates and free acid was unchanged in composition after 15 months.

The cell solutions were made by diluting the stock $Tl^{+++} + Tl^+ + SO_4^{--}$ solution to a suitable value, and adding standard A.R. sulphuric acid solution to bring the total free acid concentration to the desired value. The hydrogen electrode acid solutions were made by dilution of standard

² Watson, *J. Soc. Chem. Ind. Victoria*, 1932, 32, 679.

acid solution, which was estimated both gravimetrically (as BaSO_4) and volumetrically (titration against Na_2CO_3). All pipettes, burettes, measuring flasks, and weights were calibrated.

Redistilled mercury was further purified by passing in a fine stream of small drops through a 5-ft. column of 1 in 7 nitric acid solution about 10 times.

Mercurous sulphate was prepared by electrolysis of A.R. sulphuric acid (21 per cent. by weight in water) between a platinum cathode and an anode of purified mercury, so that about half the mercury was converted to mercurous sulphate, which formed a paste with the excess mercury. This paste was removed, left in the dark with some sulphuric acid for 14 days to reduce any mercuric sulphate present, filtered in a sintered glass Gooch crucible, washed with a little 96 per cent. alcohol, dried in air at 100°C ., and stored over calcium chloride in a desiccator shielded from light.

Cylinder hydrogen was freed from 1 per cent. of oxygen by passing through a glass tube containing a 25 cm. platinum wire electrically heated to dull redness; the gas then passed to the saturator and cell.

(b) Apparatus and Experimental Details.

The cells used (Fig. 1) were entirely of Pyrex glass. Hydrogen entered on the left by the tap A, at the rate of about 1 bubble in 5 secs. The saturator B contained the same sulphuric acid as the hydrogen electrode vessel C, through which the gas passed, emerging through the trap D, filled with the same acid. In cell (α) the Tl electrode vessel E was filled with solution, which ran through F until it just touched the ground glass

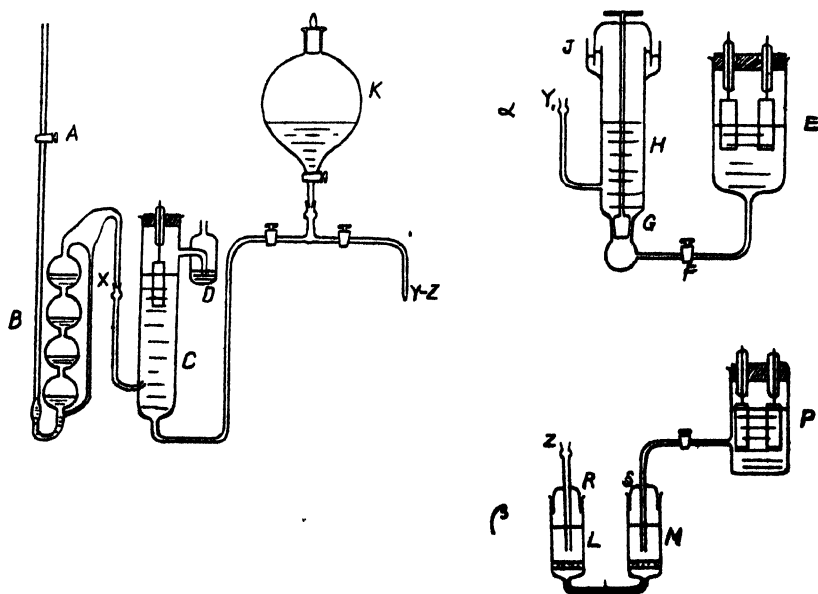


FIG. 1.

plug G, fitting into a ground socket. The plug was then fixed and sulphuric acid run into vessels C and H from the reservoir K, so that a liquid junction between sulphuric acid and sulphuric acid plus thallium sulphates was established at G. This method of establishing a cylindrically symmetrical liquid junction has been considered to give the most reproducible junction potential. The liquids were adjusted to the same level in C, H, and E, the electrodes then inserted, and H closed by pouring mercury into J.

In the cell (β) the plug junction was replaced by the double $\text{Hg} | \text{Hg}_2\text{SO}_4$ electrode vessel L-M. Mercury filled the capillary connecting L and M and about a quarter of the vessels themselves. A little mercurous sulphate, previously washed three times in the correct solution (sulphuric acid alone for L, and the mixed Tl solution for M) was added to each side. The thallium solution was run into M from the electrode vessel P, and sulphuric acid into L from the reservoir, and L and M were then closed by the greased ground-in stoppers R and S carrying the connecting tubes. Ground joints at X, Y and Z facilitated manipulation and cleaning. The cells were cleaned for each determination by immersion in chromic acid for 12 hours, followed by rinsing with tap-water, distilled water and conductivity water in turn, and finally dried in air at 130° . All taps and ground joints (except G) were greased.

The hydrogen electrodes were of platinum foil platinised thinly in pairs (as anode and cathode) from a solution of platonic chloride in hydrochloric acid (no lead salts added) for about 20 minutes, using a 4 v. accumulator and reversing the current every minute. Two bright platinum foil electrodes were used in the thallium solutions. In agreement with the observations of Abegg and Spencer, and of Grube and Hermann, it was found that if these electrodes were polarised immediately before use, the equilibrium potential was more rapidly attained, the two electrodes finally differing by no more than 0.1 mv. in any measurement, although initially the difference was 0.3 v. in some cases. Sulphuric acid of the same concentration as in the cell was electrolysed between the two platinum electrodes to polarise them, using a 2 or 4 v. accumulator, for 10 secs., the electrodes being then rinsed with some of the thallium solution used in the cell.

The cells were placed in an air thermostat at $25 \pm 0.1^\circ \text{C.}$, and were usually measured for about 8 hours, frequent barometer readings being taken. In some cases cells were observed over a period of 4 to 8 days, but no great change of E.M.F. occurred after 8 hours. The E.M.F.'s were measured to within 0.0001 v. by a Tinsley thermoelectric potentiometer, a Weston standard cell recently calibrated by the N.P.L., and a sensitive moving coil galvanometer, all the apparatus (cells, potentiometer and galvanometer) being mounted on earthed metal foil painted with insulating varnish.

A platinum wire let into the capillary joining the two $\text{Hg} | \text{Hg}_2\text{SO}_4$ electrode vessels of cell (β) provided a cell



(c) Results.

Tables I. and II. give the E.M.F.'s corrected for departure of p_{H_2} from 1 atm. The concentrations $[\text{H}_2\text{SO}_4]$, $[\text{Tl}_2\text{SO}_4]$ and $[\text{Tl}_2(\text{SO}_4)_2]$ in each cell are shown, the ratio $[\text{Tl}^+]/[\text{Tl}^{+++}] = 1.0022$ being constant throughout. Since in all the cells the hydrogen electrode is -ve, the E.M.F. of all α , β , and γ cells is by convention -ve. The values of p_{H_2} (mm. Hg) were obtained by subtracting from the corrected barometric pressures¹ the vapour pressure of water above the sulphuric acid solutions, as obtained from vapour pressure and density data.²

The observed E.M.F.'s (E obs.) were corrected to $p_{\text{H}_2} = 760$ mm. by adding the quantity

$$\Delta E = -2.303 \frac{RT}{2F} \log \frac{760}{p_{\text{H}_2}} = -\frac{59.15}{2} \log \frac{760}{p_{\text{H}_2}} \text{ mv.}$$

These E (corr.) values should also be corrected for the difference between the ratio $[\text{Tl}^{+++}]/[\text{Tl}^{++}] = 1/1.0022$ and 1, by addition of

$$\delta E = -\frac{RT}{2F} \log \frac{[\text{Tl}^{+++}]}{[\text{Tl}^{++}]} = \frac{59.15}{2} \times 0.00094 = 0.028 \text{ mv.}$$

This correction is negligibly small, and was omitted.

¹ *Int. Crit. Tables*, 1926, i., 68-70.

² *Ibid.*, iii., 56, 293.

TABLE I.—E.M.F. OF α AND β CELLS.

Cell No.	[H ₂ SO ₄] m./l.	[Ti ⁺] m./l.	[Ti ⁺⁺⁺] m./l.	P_{H_2} mm.	-E corr. v.
A1 α	1	0.03986	0.03977	740.2	1.2138
A1 β	1	0.03986	0.03977	740.4	1.1787
A2 α	1	0.009970	0.009949	740.0	1.2126
A2 β	1	0.009970	0.009949	740.0	1.2078
A3 α	1	0.001995	0.001991	739.7	1.2132
A3 β	1	0.001995	0.001991	730.6	1.2110
A4 α	1	0.0003993	0.0003984	730.6	1.2125
A4 β	1	0.0003993	0.0003984	729.9	1.2123
B1 α	0.75	0.03986	0.03977	733.3	1.2180
B1 β	0.75	0.03986	0.03977	733.7	1.1924
B2 α	0.75	0.007976	0.007959	737.9	1.2183
B2 β	0.75	0.007976	0.007959	742.3	1.2179
B3 α	0.75	0.001596	0.001593	739.5	1.2185
B3 β	0.75	0.001596	0.001593	736.9	1.2182
B4 α	0.75	0.0003194	0.0003187	737.6	1.2186
B4 β	0.75	0.0003194	0.0003187	736.8	1.2184
C1 α	0.5	0.03986	0.03977	738.2	1.2262
C1 β	0.5	0.03986	0.03977	731.1	1.1938
C2 α	0.5	0.009965	0.009944	729.2	1.2268
C2 β	0.5	0.009965	0.009944	742.1	1.2121
C3 α	0.5	0.001329	0.001327	735.8	1.2278
C3 β	0.5	0.001329	0.001327	738.1	1.2280
C4 α	0.5	0.0002660	0.0002655	736.9	1.2274
*C4 β	0.5	0.0002660	0.0002655	741.1	1.2263
D1 α	0.375	0.03986	0.03977	733.9	1.2314
D1 β	0.375	0.03986	0.03977	734.7	1.1999
D2 α	0.375	0.007976	0.007959	734.7	1.2330
D2 β	0.375	0.007976	0.007959	739.6	1.2314
D3 α	0.375	0.001596	0.001593	736.4	1.2324
D3 β	0.375	0.001596	0.001593	719.4	1.2320
D4 α	0.375	0.0003194	0.0003187	734.8	1.2319
D4 β	0.375	0.0003194	0.0003187	729.8	1.2321
E1 α	0.25	0.03320	0.03313	734.7	1.2412
E1 β	0.25	0.03320	0.03313	738.7	1.2062
E2 α	0.25	0.006643	0.006629	741.3	1.2419
E2 β	0.25	0.006643	0.006629	743.3	1.2419
E3 α	0.25	0.001329	0.001326	736.8	1.2421
E3 β	0.25	0.001329	0.001326	727.9	1.2421
E4 α	0.25	0.0002660	0.0002654	730.6	1.2416
E4 β	0.25	0.0002660	0.0002654	728.2	1.2415
F1 α	0.1	0.01329	0.01326	735.1	1.2626
F1 β	0.1	0.01329	0.01326	733.0	1.2616
F2 α	0.1	0.002659	0.002653	738.2	1.2634
F2 β	0.1	0.002659	0.002653	741.3	1.2632
F3 α	0.1	0.0005320	0.0005309	739.0	1.2629
F3 β	0.1	0.0005320	0.0005309	744.8	1.2628
F4 α	0.1	0.0001065	0.0001062	745.6	1.2621
F4 β	0.1	0.0001065	0.0001062	739.2	1.2620
*F5 α	0.1	0.00002130	0.00002126	733.3	1.2533
*F5 β	0.1	0.00002130	0.00002126	733.3	1.2621
G1 α	0.05	0.006643	0.006629	735.4	1.2777
G2 α	0.05	0.001328	0.001325	754.1	1.2797
G2 β	0.05	0.001328	0.001325	751.4	1.2798
G3 α	0.05	0.0002213	0.0002209	754.3	1.2798
G3 β	0.05	0.0002213	0.0002209	747.4	1.2795
*G4 α	0.05	0.00003689	0.00003681	742.6	1.2771
*G4 β	0.05	0.00003689	0.00003681	749.1	1.2762
H1 α	0.025	0.0003320	0.0003313	750.8	1.2952
H1 β	0.025	0.0003320	0.0003313	752.1	1.2948
H2 α	0.025	0.00005533	0.00005521	750.5	1.2932
H2 β	0.025	0.00005533	0.00005521	752.5	1.2929
*H3 α	0.025	0.000009222	0.000009202	752.4	1.2893
*H3 β	0.025	0.000009222	0.000009202	746.2	1.2898

TABLE I.—E.M.F. OF α AND β CELLS.—Continued.

Cell No.	[H ₂ SO ₄] m./l.	[Ti ⁺] m./l.	[Ti ⁺⁺⁺] m./l.	p_{H_2} mm.	—E corr. v.
I1 α	0.0125	0.00008300	0.00008282	748.0	1.3062
I1 β	0.0125	0.00008300	0.00008282	751.6	1.3060
I2 α	0.0125	0.00003320	0.00003313	755.6	1.3058
I2 β	0.0125	0.00003320	0.00003313	755.3	1.3061
I3 α	0.0125	0.000005533	0.000005521	755.9	1.2957
*I3 β	0.0125	0.000005533	0.000005521	752.6	1.2948

TABLE II.—E.M.F. OF γ CELLS.

Cell No.	[H ₂ SO ₄] m./l.	p_{H_2} mm.	—E corr. v.	Cell No.	[H ₂ SO ₄] m./l.	p_{H_2} mm.	—E corr. v.
A1	1	—	ca. 0.6720	E2	0.25	743.3	0.7136
A2	1	739.3	0.6747	E3	0.25	729.9	0.7137
A3	1	730.6	0.6747	E4	0.25	728.2	0.7136
A4	1	729.9	0.6748	F1	0.1	733.0	0.7367
B1	0.75	733.8	0.6838	F2	0.1	741.3	0.7368
B2	0.75	740.2	0.6836	F3	0.1	744.8	0.7366
B3	0.75	736.9	0.6836	F4	0.1	739.2	0.7368
B4	0.75	736.2	0.6839	F5	0.1	733.3	0.7365
C1	0.5	730.7	0.6956	G2	0.05	751.7	0.7545
C2	0.5	742.1	0.6957	G3	0.05	747.4	0.7544
C3	0.5	738.1	0.6957	G4	0.05	749.1	0.7544
C4	0.5	741.1	0.6957	H1	0.025	752.1	0.7724
D1	0.375	734.7	ca. 0.6866	H2	0.025	752.5	0.7724
D2	0.375	739.6	0.7029	H3	0.025	746.2	0.7723
D3	0.375	719.4	0.7028	I1	0.0125	751.6	0.7904
D4	0.375	729.8	0.7028	I2	0.0125	755.3	0.7906
E1	0.25	738.7	ca. 0.7117	I3	0.0125	752.6	0.7903

Table III. gives the values of E' for each concentration of sulphuric acid obtained by extrapolating the E.M.F.'s of cells α and β against $[Ti^{+++}]$ to $[Ti^{+++}] = 0$. Those cells marked * were not included, as some hydrolysis of thallic sulphate to brown thallic hydroxide had occurred in them. As may be seen, both α and β gave practically the same E' at any given acidity.

TABLE III.—VALUES OF $-E'$ V. FROM α AND β CELLS.

CH ₃ SO ₄	1	0.75	0.5	0.375	0.25	0.1	0.05	0.025	0.0125
α	1.2124	1.2187	1.2272	1.2318	1.2415	1.2628	1.2785	1.2925	1.3057
β	1.2124	1.2185	1.2272	1.2322	1.2414	1.2627	1.2775	1.2923	1.3061
av.	1.2124	1.2186	1.2272	1.2320	1.2415	1.2628	1.2780	1.2924	1.3059

Table IV. gives the average E.M.F. of the γ cell for each sulphuric acid concentration. The close agreement of individual measurements with a given solution is evidence of the great degree of reproducibility of the hydrogen and Hg | Hg₂SO₄ electrodes.

TABLE IV.—AVERAGE E.M.F. OF γ CELL.

CH ₃ SO ₄	1	0.75	0.5	0.375	0.25	0.1	0.05	0.025	0.0125
—E v.	0.6747	0.6837	0.6937	0.7028	0.7136	0.7367	0.7544	0.7724	0.7904

These values (Fig. 2) agree excellently with those published by previous workers* in spite of the intentional neglect of the precautions to exclude oxygen from the cell usually adopted.

* Wilmore, *Z. physik. Chem.*, 1900, **35**, 290; Luther and Pokorny, *Z. anorg. Chem.*, 1907, **57**, 290; Brønsted, *Z. physik. Chem.*, 1910, **68**, 693 (interpol.); Edgar, *Thesis*, Mass. Inst. Tech., Boston, 1912; Lewis and Lacey, *J.A.C.S.*, 1914, **36**, 804; Randall and Cushman, *J.A.C.S.*, 1918, **40**, 393; Harned and Sturgis, *J.A.C.S.*, 1925, **47**, 945; Bircher and Howell, *J.A.C.S.*, 1926, **48**, 34; Harned and Hamer, *J.A.C.S.*, 1935, **57**, 27.

Discussion.

If, in (5), a_{H^+} is replaced by $2cf_{H^+}$ we have

$$E' - \frac{RT}{F} \log_e 2c = E_0 - \frac{RT}{2F} \log_e \frac{f_{Tl^{+++}} c_{Tl^{+++}}}{f_{Tl^+} c_{Tl^+}} + \frac{RT}{F} \log_e f_{H^+} \quad (6)$$

If the quantity on the left is extrapolated against $c^{\frac{1}{2}}$ to $c = 0$, the activity coefficients $f_{Tl^{+++}}$, f_{Tl^+} and f_{H^+} all become equal to 1, and since

$c_{Tl^+} = c_{Tl^{+++}}$, the logarithmic terms on the right vanish, leaving E_0 , which can thus be obtained without any calculations of liquid contact potentials. The extrapolation, which is rather uncertain, leads to the approximate value $E_0 = -1.20$ v. Extrapolation against $\mu^{\frac{1}{2}}$ as calculated by the method of Shrawder and Cowperthwaite¹⁰ on the assumption that only the first stage dissociation of sulphuric acid is complete and the dissociation constant of the

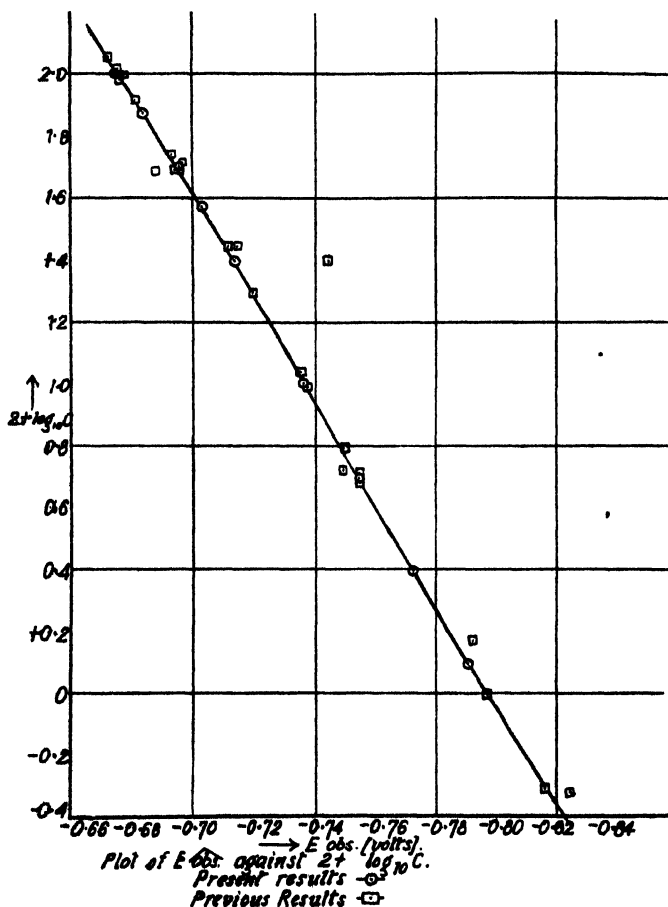


FIG. 2.

HSO_4' ion is 0.0120 at 25° ¹¹ leads to the value $E_0 = -1.1982$ v. Further, for the two most dilute sulphuric acid solutions used, the values of μ and α (degree of dissociation of HSO_4') can be obtained by the method of Shrawder and Cowperthwaite, and thence the actual concentration $c_{H^+} = c(1 + \alpha)$ of H^+ ion calculated. f_{H^+} can be obtained by the use of the La Mer equation, on the assumption that f_{H^+} has the same value as the mean activity coefficient of a 1:1 type electrolyte,

¹⁰ J.A.C.S., 1934, 56, 2340.

¹¹ Hamer, J.A.C.S., 1934, 56, 860.

and by taking the value of 'a' as = 3.64 Å., which seems a likely value for H_2SO_4 (cf. the values 3.6 for CdSO_4 and 3.64 for ZnSO_4). Then $f_{\text{H}^+} c_{\text{H}^+} = a_{\text{H}^+}$, and if

$$E' - \frac{RT}{F} \log_e a_{\text{H}^+}$$

in (5) is extrapolated against μ^\dagger to $\mu = 0$, E_0 is obtained. The calculated values are given in Table V., and the assumption of a linear relation between $(E' - \frac{RT}{F} \log_e a_{\text{H}^+})$ and μ^\dagger gives, on extrapolation, $E_0 = -1.1992$ v.

TABLE V.

$c(\text{H}_2\text{SO}_4)$	α	μ^\dagger	c_{H^+}	$-\log f_{\text{H}^+}$	$-\frac{RT}{F} \log a_{\text{H}^+}$	$-(E' - \frac{RT}{F} \log_e a_{\text{H}^+})$
0.025	0.4661	0.2198	0.03665	0.09875	0.0908 v.	1.2016 v.
0.0125	0.5890	0.1650	0.01986	0.07079	0.1049 v.	1.2010 v.

This is as far as it is possible to go without the calculation of liquid contact potentials. We now proceed to calculate a_{H^+} for various concentrations of sulphuric acid by a method involving such potentials and based on the work of Ferguson and France.¹² Let

$$E_{\text{H}} = \text{E.M.F. of the cell Pt, H}_2 \mid \text{H}_2\text{SO}_4 (c_1) \mid \text{H}_2\text{SO}_4 (c_2) \mid \text{H}_2, \text{Pt,}$$

$$E_1 = \text{E.M.F. of the cell Pt, H}_2 \mid \text{H}_2\text{SO}_4 (c_1) \mid \text{Hg}_2\text{SO}_4, \text{Hg,}$$

$$E_2 = \text{E.M.F. of the cell Pt, H}_2 \mid \text{H}_2\text{SO}_4 (c_2) \mid \text{Hg}_2\text{SO}_4, \text{Hg,}$$

and

$$E = E_1 - E_2.$$

Then, by treating sulphuric acid as a 2 : 1 type electrolyte and using concentrations instead of activities, we have, approximately,

$$\begin{aligned} E_{\text{H}} &= \text{alg. sum of electrode potentials} - E_{\text{L}} \\ &= \frac{RT}{F} \log_e \frac{c_1}{c_2} - \frac{2u_o - u_a}{2(u_o + u_a)} \frac{RT}{F} \log_e \frac{c_1}{c_2} \\ &= \frac{3}{2} \frac{u_a}{u_o + u_a} \frac{RT}{F} \log_e \frac{c_1}{c_2}, \quad \dots \quad (7) \end{aligned}$$

where E_{L} , the opposing liquid contact potential, is expressed in terms of the anionic and cationic mobilities, u_o and u_a respectively, by the Nernst equation. Similarly :

$$E = \frac{3}{2} \frac{RT}{F} \log_e \frac{c_1}{c_2}. \quad \dots \quad (8)$$

By eliminating $\log_e (c_1/c_2)$ between (8) and the expression for E_{L} we find

$$E_{\text{L}} = E \frac{2u_o - u_a}{3(u_o + u_a)}, \quad \dots \quad (9)$$

or, since the transport number n_o is $u_o/(u_o + u_a)$, we have

$$E_{\text{L}} = E \frac{3n_o - 1}{3}. \quad \dots \quad (10)$$

The algebraic sum of the electrode potentials in (7) is strictly

$$\frac{RT}{F} \log_e \frac{(a_{\text{H}^+})_1}{(a_{\text{H}^+})_2},$$

and thus on substituting for E_H and E_L in terms of E by means of (7), (8) and (10), we find :

$$\frac{RT}{F} \log_e \frac{(a_H^+)_1}{(a_H^+)_2} = E \left(1 - n_e + \frac{3n_e - 1}{3} \right) = \frac{2}{3}E. \quad (11)$$

The values of E between any pair of values of c_1 and c_2 can be read from the graph of the E.M.F. of γ cells against c , and inserted in (11) to obtain values of $\frac{RT}{F} \log_e [(a_H^+)_1/(a_H^+)_2]$. These are given in Table VI. together with the values of E_L calculated from (10). The values of n_e , also included in the table, were chosen from the available data.¹³ The values of E_L from (10), indicated by "F F" in Table VI., may be compared with those obtained by Henderson's formula.¹⁴ In the present case, if complete dissociation of sulphuric acid to $2H^+ + SO_4^{2-}$, and practical constancy of n_e over a small range of concentration are assumed, this reduces to

$$E_L = \frac{RT}{F} \frac{2n_e - 1}{2 - n_e} \log_e \frac{c_1}{c_2}. \quad (12)$$

The latter values, designated "Hend." in the Table, do not differ considerably from the former and it is reasonable to suppose that some reliance may be placed on the tabulated values of

$$\frac{RT}{F} \log_e [(a_H^+)_1/(a_H^+)_2].$$

TABLE VI.—VALUES OF E_L AND $\frac{RT}{F} \log_e [(a_H^+)_1/(a_H^+)_2]$ IN V.

c_1	c_2	$-E_1$	$-E_2$	$-E$	E_H	n_e	$-E_L$		$-\frac{RT}{F} \log_e \frac{(a_H^+)_1}{(a_H^+)_2}$
							FF.	Hend.	
1.0	0.5	0.6747	0.6957	0.0210	0.0042	0.801	0.0098	0.0089	0.0140
1.0	0.75	0.6747	0.6837	0.0090	0.0018	0.800	0.0043	0.0037	0.0060
0.5	0.25	0.6957	0.7136	0.0179	0.0035	0.805	0.0085	0.0091	0.0120
0.75	0.375	0.6837	0.7028	0.0191	0.0038	0.803	0.0091	0.0090	0.0127
0.5	0.1	0.6957	0.7367	0.0410	0.0078	0.809	0.0195	0.0215	0.0273
0.1	0.01	0.7367	0.7970	0.0603	0.0113	0.8132	0.0289	0.0312	0.0402
0.5	0.05	0.6957	0.7544	0.0587	0.0110	0.8132	0.0281	0.0312	0.0391
0.05	0.005	0.7544	0.8160	0.0616	0.0115	0.8132	0.0296	0.0312	0.0411
0.05	0.025	0.7544	0.7724	0.0180	0.0034	0.8132	0.0086	0.0094	0.0120
0.025	0.0125	0.7724	0.7904	0.0180	0.0034	0.8132	0.0086	0.0094	0.0120

Since these calculations were completed, a new set of values of n_e has appeared¹⁵ which differ from those used. Equation (11) shows, however, that

$$\frac{RT}{F} \log_e [(a_H^+)_1/(a_H^+)_2]$$

is independent of n_e . Recalculation of E_L with the new n_e values introduces differences of only a few tenths of 1 mv., even at the higher concentrations.

The arbitrary assumption that $a_H^+ = 1$ when $c = 1$ (which is pro-

¹³ Ferguson and France, *loc. cit.*; *Int. Crit. Tables*, 1929, vi., 310.

¹⁴ *Z. physik. Chem.*, 1906, 59, 118; 1908, 63, 325.

¹⁵ Hamer, *J.A.C.S.*, 1935, 57, 662.

bably not far from the truth)¹⁶ gives the following relative values of $\frac{RT}{F} \log_e a_{H^+}$ from the values of $\frac{RT}{F} \log_e [(a_{H^+})_1/(a_{H^+})_2]$:

c	1.0	0.75	0.5	0.375	0.25	0.1	0.05	0.025	0.0125	0.005
$-\frac{RT}{F} \log_e a_{H^+} + v.$	0	0.0060	0.0140	0.0187	0.0260	0.0413	0.0531	0.0651	0.0771	0.0942

These values are probably reliable to within 1 mv. It only remains to find the absolute value of a_{H^+} for any one value of c . This might be done by extrapolating the values of $\frac{RT}{F} \log_e f_{H^+}$ (obtained by subtracting $\frac{RT}{F} \log_e 2c$ from the values of $\frac{RT}{F} \log_e a_{H^+}$) against $c^{\frac{1}{2}}$ to $c = 0$, and hence $f_{H^+} = 1$. The extrapolation is, however, uncertain, giving for $c = 1$ only the very approximate value $\frac{RT}{F} \log_e a_{H^+} = -0.035$ v., which is

not sufficiently accurate for present requirements. A better value may be obtained as follows. A consideration of existing data,¹⁷ in which -0.3334 v. is taken for the potential of the $N/10$ calomel electrode referred to the standard hydrogen electrode, leads us to consider that the potential of the electrode $Hg | Hg_2SO_4, N-H_2SO_4$ at 25° is -0.6736 v. This is subject to an uncertainty of about 0.0060 v., since two values of the temperature coefficient of the N -calomel electrode, namely, -0.0061 v./ $^\circ C$.¹⁸ and $+0.0024$ v./ $^\circ C$.¹⁹ have been proposed.

With this value, and the E.M.F. of the cell $Hg | Hg_2SO_4, H_2SO_4$ (0.5 mol./lit.), H_2 , Pt: $E = -0.6957$ v. at 25° , we obtain for the electrode Pt, H_2/H_2SO_4 (0.5 mol./lit.) the potential $+0.0221$ v. at 25° . Thus, for $c = 0.5$, $RT/F \log_e a_{H^+} = -0.0221$ v.

Since there is an uncertainty of 0.0060 v., an independent evaluation is desirable, and may be obtained from the following cells, measured at 25° by Wilsmore:—

(i) $Hg | HgCl, KCl$ (1 m./l.) $| H_2SO_4$ (0.5 m./l.) $| H_2$, Pt, $E = -0.3276$ v.

(ii) $Hg | HgCl, KCl$ (0.5 m./l.) $| H_2SO_4$ (0.5 m./l.) $| H_2$, Pt, $E = -0.3516$ v.

Fales and Mudge²⁰ obtained the following potentials at 25° for the calomel electrode with various KCl concentrations, reckoned on an arbitrary standard.

	KCl conc. (mol./lit.)	$-E$ v.
On the basis $E = -0.3334$ v. for $c_{KCl} = 0.1$ mol./lit., the potentials of the calomel electrodes in Wilsmore's cells (i) and (ii) are:	0.1	0.6177
(i) -0.2809 v.	0.5	0.5808
(ii) -0.2967 v.	1.0	0.5648

The liquid contact potentials, which act by flow of positive electricity in the direction of the arrow *inside* the cell, may be calculated by Henderson's formula on the assumption of complete dissociation of KCl and with ionic mobilities calculated from the equivalent conductivities and transport numbers²¹:—

¹⁶ Kunz, *J.A.C.S.*, 1931, **53**, 98.

¹⁷ Glover, *J.C.S.*, 1933, 10; Wilsmore, *Z. physik. Chem.*, 1900, **35**, 290; Glasstone, *Electrochemistry*, pp. 292 f.

¹⁸ Glover, *J.C.S.*, 1933, 10.

¹⁹ Clark, *The Determination of Hydrogen Ions*, 1928, chap. xii.

²⁰ *J.A.C.S.*, 1920, **42**, 3434.

²¹ *Int. Crit. Tables*, 1929, vi., pp. 234, 242-extrap. for H_2SO_4 .

H_2SO_4 0.5 mol/lit.	KCl 1.0 0.5 mol/lit.
$A(\frac{1}{2}\text{H}_2\text{SO}_4)$ 212.5 mhos.	$A(\text{KCl})$ 111.86 117.2 mhos.
n_0 0.803	n_0 0.496 0.496

The assumption of complete dissociation of H_2SO_4 to $2\text{H}^+ + \text{SO}_4^{2-}$ gives the contact potentials (i) 0.0192 v. and (ii) 0.0249 v. The more probable assumption (*cf.* Shrawder and Cowperthwaite) that only the first dissociation into H^+ and HSO_4^- occurs completely, gives the potentials (i) 0.0212 v. (Glover's value is 0.023 v.), and (ii) 0.0278 v. The latter values with results from cells (i) and (ii), give the following values for the electrode potential at 25° of $\text{Pt}, \text{H}_2 | \text{H}_2\text{SO}_4$ (0.5 mol/lit.):

$$\begin{aligned} \text{(i)} \quad & 0.3276 - 0.2809 - 0.0212 = 0.0255 \text{ v.} \\ \text{(ii)} \quad & 0.03516 - 0.2967 - 0.0278 = 0.0261 \text{ v.} \end{aligned}$$

The average value, 0.0258 v. (with a probable error of a few tenths of 1 mv.) is in fair agreement with the previous value 0.0221 (with an uncertainty of 0.0060 v.).

This electrode potential is equal to $-\frac{RT}{F} \log_e a_{\text{H}^+}$ in sulphuric acid of $c = 0.5$ mol/lit., so that the relative values of the latter may be referred to the standard hydrogen electrode, and in accordance with (5), by adding these standard values of $-\frac{RT}{F} \log_e a_{\text{H}^+}$ to the values of E' we obtain values of the oxidation-reduction potential E_x for zero TI content referred to the standard hydrogen electrode, as given below:

c	1.0	0.75	0.50	0.375	0.25	0.1	0.05	0.025	0.0125
$\frac{RT}{F} \log_e a_{\text{H}^+} \text{ v.}$	0.0118	0.0178	0.0258	0.0305	0.0378	0.0531	0.0649	0.0769	0.0889
$-E_x - \text{I v.}$	0.2006	0.2007	0.2014	0.2017	0.2037	0.2097	0.2131	0.2155	0.2170

By extrapolating either E_x or $\log(-E_x - \text{I})$ against $c^{\frac{1}{2}}$ to $c = 0$, the value $E_0 = -1.2207$ v., with an uncertainty less than 1 mv., is obtained. Extrapolation against $\mu^{\frac{1}{2}}$, as in Table V., on the assumption of a linear relation between E_x and $\mu^{\frac{1}{2}}$, leads to a value numerically only 0.5 mv. larger. Although this value of E_0 differs from that obtained on p. 1367 without the introduction of liquid contact potentials, it is to be preferred to the latter, because it is referred to the standard of the hydrogen electrode in hydrochloric acid of mean activity 1, whereas the previous value is referred to the hydrogen electrode in sulphuric acid for which $a_{\text{H}^+} = 1$, and also involves uncertain values of $\mu^{\frac{1}{2}}$ and f_{H^+} for sulphuric acid.

The values given explain why previous investigators concluded that the acid concentration has little or no effect on E_x , since in the range 1.0 to 0.25 for c , E_x changes by only 2 or 3 mv. On further decrease of c , however, greater changes in E_x occur.

The numerical discrepancy between the new value of E_0 (-1.2207 v.) and that of Grube and Hermann (-1.204 v. when corrected), is greater than would be expected from the difference of working temperatures alone, and the present values of E_x are seen to increase numerically with decrease of c , while the reverse is the case with the E_0 values of Grube and Hermann. Equation (5) shows that for $[\text{TI}^+] = [\text{TI}^{+++}]$, we have:

$$E_x = E' - \frac{RT}{F} \log_e a_{\text{H}^+} = E_0 - \frac{RT}{F} \log_e \frac{f_{\text{TI}^{+++}}}{f_{\text{TI}^+}},$$

or
$$-\log_{10} \frac{f_{\text{TI}^{+++}}}{f_{\text{TI}^{+}}} = (E_{\infty} - E_0)/0.05915, \quad (13)$$

Some values of $-\log_{10} \frac{f_{\text{TI}^{+++}}}{f_{\text{TI}^{+}}}$ calculated from (13) are given below:

c	0.1	0.05	0.025	0.0125
$-\log_{10} \frac{f_{\text{TI}^{+++}}}{f_{\text{TI}^{+}}}$	0.1860	0.1284	0.0879	0.0626

The La Mer equations have not been developed for the case of single ions, but the Debye-Hückel equation can be applied, with the same value of ' a ' for both ions, in the form:

$$-\log \frac{f_{\text{TI}^{+++}}}{f_{\text{TI}^{+}}} = \frac{h\sqrt{\mu}}{1 + g \cdot a\sqrt{\mu}}(9 - 1) = \frac{8h\sqrt{\mu}}{1 + g \cdot a\sqrt{\mu}}.$$

From this it is seen that as μ (or the H_2SO_4 concentration) increases, the value of $-\log \frac{f_{\text{TI}^{+++}}}{f_{\text{TI}^{+}}}$ also increases, *i.e.*, E_{∞} becomes increasingly positive, or decreases numerically. This result, which supports the present values and disagrees with those of Grube and Hermann, is actually independent of the Debye-Hückel equation, since at the concentrations involved it is known that $-\log f$ for any ion is greater the higher its valency (at any given μ), and increases with rise of μ .

The Debye-Hückel equation with the value ' a ' = 3.64 Å., and the values of μ from Table V., gives for $-\log \frac{f_{\text{TI}^{+++}}}{f_{\text{TI}^{+}}}$ the values 0.7804 for $c = 0.025$, and 0.5583 for $c = 0.0125$. These figures are quite different from those just found, and the Debye-Hückel theory does not seem to apply to the present results. Activity coefficients for the single ions interpolated from the data of Lewis and Randall²² give values of $-\log \frac{f_{\text{TI}^{+++}}}{f_{\text{TI}^{+}}}$ of 0.4225 for $c = 0.025$ and 0.3772 for $c = 0.0125$, which again are unsatisfactory and indicate either that Lewis and Randall's values for the activity coefficients of trivalent ions are inaccurate, or that they do not apply to the TI^{+++} ion. The latter conclusion seems to be indicated by the results of Popoff and Kunz⁶ who found that these activity coefficients for trivalent ions, when applied to Fe^{+++} , gave values of E_0 with an equation of the form (13) which were approximately equal to that obtained by extrapolation.

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²² *Thermodynamics*, 1923, p. 382.

REVIEWS OF BOOKS.

The Discovery of Specific and Latent Heats. By D. McKIE and N. H. DE V. HEATHCOTE. (London: E. Arnold & Co. 1935. Pp. 155. Price 6s. net.)

THE history of the discovery of specific and latent heats has been very obscure, since, even if Cavendish's contributions are omitted, the question of the shares of Black and of Wilcke, and the possibility of plagiarism by the latter, remain for consideration. The discussion by Robison in his edition of Black's *Lectures* is a very important document, which deserves perhaps more confidence than the present authors seem willing to admit, since it undoubtedly represents traditions descending from Black himself, including the suggestion of plagiarism. It is, of course, quite possible that Black's own views, which Robison transmits and amplifies, may have been wrong, and it is the duty of the historian to consider the matter in the light of all the material, which is what has been very ably done by the present authors. Their main conclusion justifies the claim put forward on behalf of Black as the originator in the matter, but they seem to clear Wilcke from the charge of intentional plagiarism. The various original sources have been carefully examined, including memoirs in Swedish, and the very obscure methods of calculation used in some cases are explained. The book is a substantial contribution to literature on the history of science.

J. R. P.

The Chemistry of Cement and Concrete. By F. M. LEA, M.Sc., A.I.C., and C. H. DESCH, D.Sc., Ph.D., F.R.S. (London: Arnold & Co. Pages 429. Price, 25s. net.)

Writing as one who has taken a deep interest in the manufacture of Portland cement in this country, and been actively engaged in its production from the pre-rotary days, the reviewer has always had the feeling that the chemist-in-charge of the operations involved has not been at all well supported by the research side. Such books as have hitherto been published in this country on the subject of Portland and other cements have dealt too much with, so to say, the beaten track of knowledge, *i.e.*, the machinery and plant required, outputs to be expected from certain types of machines, and the tests to be carried out on the finished product with details of specifications—the daily avocation of the chemist and manager.

Some of us did expect that when the important cement companies joined together to carry out research work, they would pursue it thoroughly, and once again place this country in the forefront of knowledge on this subject; as should rightly be, seeing that we were the pioneers of the industry.

It has remained, however, for these two authors to come forward and not only give us the benefit of their scientific experience, but also embody the latest conclusions of the most expert cement chemists abroad. This is, one can say definitely, the best and only standard work we have on this subject dealing with every phase of cement production and the chemical

reactions which take place; the most important feature from the users' standpoint is the thorough way in which the authors have discussed the lateral developments of cement, such as white cement, coloured cement, aluminous cement, etc., and the effects of admixtures, and this section should be read carefully when certain trade specialities are being considered with the object of hardening or waterproofing the concrete.

The book, whilst appealing to all those directly concerned in the manufacture of cement or cement products (as it enables the enquirer to have at his command now, all the information of any account) will also appeal to a wider field, if only for the practical knowledge on the utility of the various cements and concrete when in contact with destructive agencies. This is important to the architect as well as to the constructional engineer, and for this reason, if for no other, the book should be studied and retained as a work of reference, if the advice given is acted upon, then we shall not hear so much of concrete failures in the future. Tensile or compressive strength in cement is, as the authors rightly point out, not the only consideration that matters; if we are to have confidence in the concrete, more safeguards will have to be insisted upon in the specification, since tests which have just come to hand show that Portland cement concrete subjected to the action of soft water during the past twelve months has been considerably attacked and even perforated.

The publishers are to be congratulated on issuing the volume in such a handsome form at so moderate a price. The book is easy to read on account of the clear type.

JAMES WATSON.

Sound. By E. G. RICHARDSON. (London, Edward Arnold & Co. Second Edition, 1935. Pages iv + 319. Price nett.)

The second edition of Dr. Richardson's treatise has been enlarged by the addition of chapters on impedance, supersonics and the reproduction of sound. The new matter preserves the traditions of clarity and thoroughness which characterised the old edition and, while the book may still be called elementary in that it makes no great use of advanced mathematics, it is advanced enough to be regarded as a treatise which will bring an honours student into touch with the problems of modern research and leave him with nothing to unlearn.

The bibliographies are full and up-to-date and the book may be unreservedly commended.

But what is Laplace doing in the *Ann. d. Physik*?

A. F.

Lehrbuch der physikalischen Chemie. 1st part of 5th vol. by Dr. KARL JELLINEK. (Stuttgart: Ferdinand Enke. Pp. 288 + 127 diagrams. 1935. Price R.M. 27).

This text book has now reached the fifth and last volume and includes sections on the surface phenomena of mixtures, chemical kinetics, electrolysis, and the structure of matter (pp. 18 unfinished). That on surface phenomena covers monomolecular layers, the Gibbs equation, the electrical properties of disperse systems and colloid chemistry. The book on

chemical kinetics occupies one half of the volume and deals with experimental and theoretical work on gaseous, liquid, and solid systems. The section on electrochemistry is a compilation of the principal facts on electrolysis, over-voltage, passivity, etc.

The author covers a good deal of ground in this section of his text-book and this he achieves by making a selection of the more important material in such a way as to leave no very obvious gaps. The method has the advantage of giving a broad survey of the field without sacrificing any relevant detail in the parts with which he treats. The older and modern work are closely incorporated in the argument and the impression given is that of a view seen in perspective. The author has succeeded in rediscovering the lost art of text-book writing. Ultra modern and more speculative views do not find a place in this book. For example, there is no extended theory of monomolecular reactions and very little on chain reactions. The work is in essence a text-book and not a monograph.

Numerous references are given to the original literature and to other text-books and monographs.

W. E. G.

The Fundamentals of Chemical Thermodynamics. Part I. Elementary Theory and Electrochemistry. By J. A. V. Butler. London: (Macmillan & Co. Pp. xi + 253. 1935. Price 7s. 6d.)

The new edition of this work contains some alterations in arrangement and some additional sections. The latter include electrolysis, oxidation-reduction indicators, hydrogen and glass electrodes and some less important sections. The book mostly follows closely the lines of Lewis and Randall and even the illustrative examples are mostly American. Answers to most of the examples are given in this edition, which is a distinct improvement on the first. The book includes the theory of a number of processes and instruments now in common use in industry or in the laboratory, and should be found very useful.

J. R. P.

Molekülspektren und ihre Anwendung auf Chemische Probleme. I. Tabellen. By H. SPONER. (Berlin: Julius Springer. Pp. vi + 154. 1935. Price 16 RM. [Paper covers]. 17.40 R.M. [Bound]).

This book contains the tabular matter for the main portion of the whole work, which is to follow. Five sections go to make up the contents, (1) Constants for the spectra of diatomic molecules, (2) Data for infra-red and Raman Spectra of poly-atomic molecules, (3) Data for Electronic Spectra of poly-atomic molecules, (4) Data for Electronic collision processes in molecules, and finally, an Appendix. An excellent index of substances is included.

A valuable feature is that each section is provided with a brief introduction, giving in outline the nature of the spectrum in question and its origin. It remains to add that the format is fully up to the high standard expected of Springer publications.

F. I. G. R.

DIABATIC REACTIONS AND PRIMARY CHEMILUMINESCENCE.

By R. A. OGG, JUN., AND M. POLANYI.

Received 4th July, 1935.

Ionogenic Reactions.

A theory of chemical reactions in which atoms are converted into ions has been put forward by the authors. The atoms under consideration can be either free or bound in a homopolar bond, the ions also, either free or bound in ionic molecules.

The theory has been outlined in a general form in a preliminary communication,¹ and some specific applications and further generalisations have been already published or are in the course of publication. To these we will briefly turn later.

Our present argument requires reference to an explicit statement of the theory in its general form. We shall have to give this here, since such a statement has not so far been published.

Suppose we have three reacting particles, for example



where R signifies an organic radical of which a carbon atom is linked to the Cl. We have then on the left of the formula, a homopolar state, whilst the right includes the ionic molecule NaCl.

The method consists in calculating two alternative energy surfaces corresponding respectively to the homopolar state on the left and the ionic state on the right.* The configuration of the three particles involved being assumed to be throughout collinear, both surfaces are two-dimensional and depend on the same two co-ordinates, namely (a) the separation of the particles Na and Cl, and (b) the separation between the Cl-atom and the carbon atom connected with Cl in the radical R. We term these two co-ordinates the separations (Na . . . Cl) and (Cl . . . R), and we call the two energy-surfaces the surfaces [Na . . . Cl . . . R]_h and [Na . . . Cl . . . R]_i, the subscripts indicating the homopolar and ionic state respectively.

The calculation of $[\text{Na} \dots \text{Cl} \dots \text{R}]_h$ offers, in principle, no new problem. London's equation for three atoms, in combination with spectroscopic data as utilised by Eyring and Polanyi, is available for this purpose. To determine $[\text{Na} \dots \text{Cl} \dots \text{R}]_i$ we must have the potential curve of the NaCl molecule and also we must estimate the forces (chiefly repulsive) between the Cl^- ion and R. The former point

¹ *Manchester Lit. Phil.*, 1933-34, 78, 41.

* The technique of using an energy-surface is based on the paper of Eyring and Polanyi, *Z. physik. Chem.*, 1931, B 12, 279.

offers no great difficulty, the treatment of a problem involving the latter point has been put forward in detail in a previous communication.²

It will be remembered that the energy surface of a homopolar system of three atoms forms two "valleys," those of the initial and the final states, between which lies a "saddle." Such will be the general form of $[\text{Na} \dots \text{Cl} \dots \text{R}]_h$, but the "final state-valley," corresponding to a homopolar NaCl molecule and a free R radical, will not be the true final state of the reaction as represented by equation (1). The true "final state valley" is represented on the $[\text{Na} \dots \text{Cl} \dots \text{R}]_i$ surface for which the NaCl is ionically bound. The energy of this valley lies far below the spurious "final state valley" of the $[\text{Na} \dots \text{Cl} \dots \text{R}]_h$ surface.

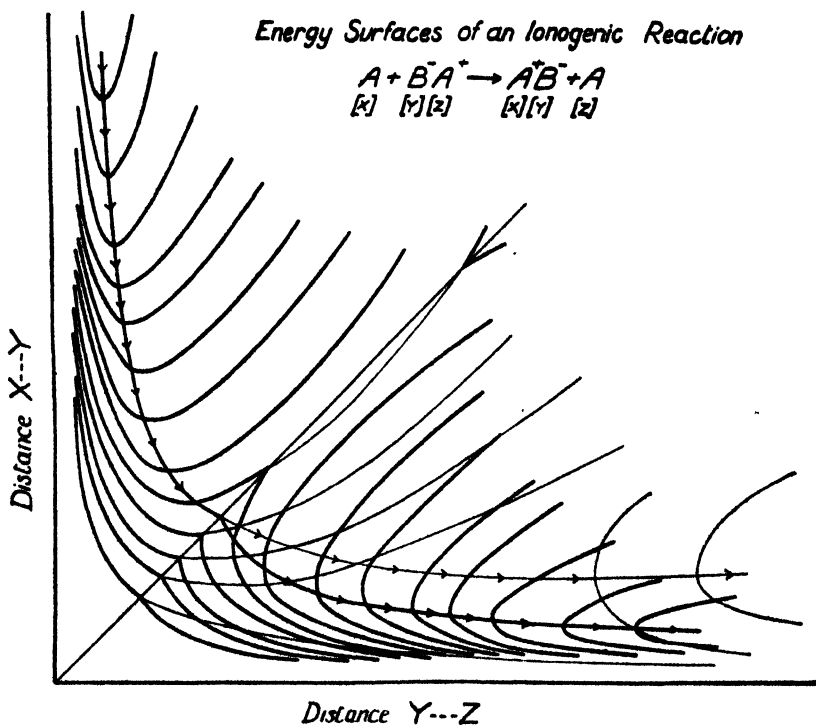


FIG. 1.

Conversely, there exists also a very shallow valley representing the initial state of the ionic surface. It is the state in which the Na^+ ion is free and a Cl^- ion and the radical R are attached to one another by weak Van der Waals' forces. Obviously, the energy of this valley lies far above the energy level of the homopolar "initial state valley," which actually represents the reactants on the left of equation (1).

The reaction (1) is thus found to be a transition from the "initial state valley" of the surface $[\text{Na} \dots \text{Cl} \dots \text{R}]_h$ to the "final state valley" of the surface $[\text{Na} \dots \text{Cl} \dots \text{R}]_i$. It follows that the two surfaces cross each other. The line of intersection of the two surfaces represents.

² *Trans. Faraday Soc.*, 1935, 31, 604.

all possible transition states between the (initially) homopolar and the (finally) ionic states of the reacting particles.

A diagram showing how two energy surfaces corresponding to two different electronic states cross each other is presented in Fig. 1. The reaction is supposed to be a "symmetrical" one such as, e.g.,



The parts of the surfaces drawn in thick lines correspond to the true initial and final states, i.e. when NaCl is in the ionic state. The thin lines show the continuation of the contours of the initial state, the system passing over into the spurious final state of an $\text{Na} \dots \text{Cl}^-$ particle with Na^+ removed to infinity. No attempt has been made to approximate the true magnitudes of the case.

The two surfaces are seen to cross each other in a line which in the projection shown in the figure is the diagonal.

All application of this approach has been hitherto made in those cases where the spurious "final state valley" of the homopolar surface lies far above the valley representing the true (ionic) final state. Supposing further, that the transition from the homopolar surface to the ionic surface at the intersection line is not restricted to any considerable extent (*vide infra*), we can then assume that:

- (a) The reaction will occur in a state represented by a point on the intersection line.
- (b) There is along the "reaction path" no energy value exceeding the energy value of this point, and it will follow further that
- (c) The point representing the actual transition state will be the point of the intersection line having the lowest energy value, and
- (d) The activation energy* is represented by the energy value of this lowest point of the intersection line.

To calculate the activation energy, this lowest point on the line of intersection has to be found.

A general view of the theory can be given by a two-dimensional diagram (Fig. 2) in the following way:

We firstly represent a plane section of both surfaces going through the lowest point of their intersection

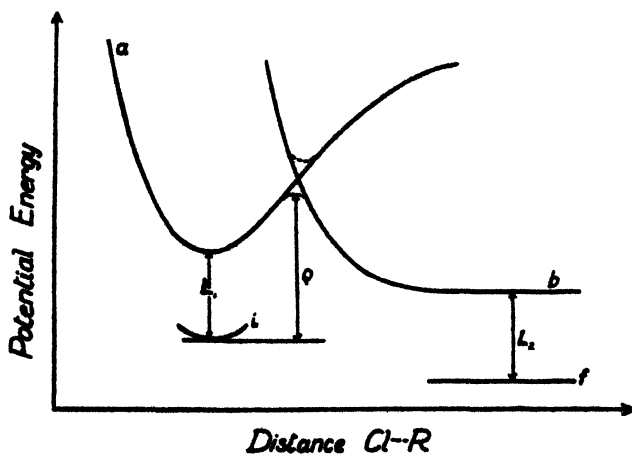


FIG. 2.

line, i.e. through the transition state of the reaction. Following the precedent given in an earlier paper, we chose the plane which is defined by a constant separation of the "attacking" free particle and the

* Or its upper limit (*vide infra*).

"attacked" atom. In the case of reaction (1) this leads to a plane for which $(\text{Na} \dots \text{Cl}) = \text{constant}$; the value of the constant being the value of the separation $(\text{Na} \dots \text{Cl})$ in the transition state. We called this distance formerly the "critical value" of the $(\text{Na} \dots \text{Cl})$ separation: $(\text{Na} \dots \text{Cl})_{\text{crit.}}$

Such a section as shown in Fig. 2 is composed of two curves, (a) and (b), referring respectively to the homopolar and the ionic states. Curve a represents the potential curve of a Cl—R bond under the influence of the proximity of an Na atom; curve b is the repulsive curve between Cl^- and R (slightly influenced by the presence of the Na^+ ion).

We can further introduce the energy levels of the initial and final states. They are given by the curves (i) and (f) respectively. Curve (i) gives the lower part of a potential curve of the Cl—R bond, which is in no way influenced by the Na-atom, since this is at infinity; (f) gives the level of the final state of the reaction.

The energy L_1 represents the work to be expended to bring the Na atom to the critical distance $(\text{Na} \dots \text{Cl})_{\text{crit.}}$; L_2 is the energy evolved when, after the reaction has been completed whilst $(\text{Na} \dots \text{Cl})_{\text{crit.}}$ was kept constant, the newly formed NaCl molecule is left to relax into its natural equilibrium state. The values of the abscissæ of the curves (i) and (f) have no physical meaning, they are chosen to fit into the picture.

Actually, according to the theorem of Neumann and Wigner the "crossing" curves (a) and (b) never cross each other. The true conditions are better represented by the dotted curves, the separation of which is the perturbation energy (W) at the "crossing." We will refer to this later.

At the moment we only wish to point out, that if the system passes over from curve a to curve b along the dotted curve connecting them, the activation energy will be found to be Q as shown in the diagram.

We note that the transition along the dotted line will invariably take place if the motion of all particles is infinitely slow, or their masses infinitely large. This is, therefore, to be called an *adiabatic* process.

As opposed to the adiabatic transition there is the important possibility of a transition crossing the gap between the dotted curves. This is the non-adiabatic transition, to be expected for swift particles of light mass or else in such cases where the gap (W) between the curves is particularly small. For ordinary reactions, (non-photochemical), W has to be of the order of kT to make the non-adiabatic process probable to an appreciable extent³ (*vide infra*).

In this paper we propose to make use of the shorter term "diabatic" instead of "non-adiabatic."

The treatment as given above for a change over from a homopolar to an ionic state can be applied to electrolytic dissociation, e.g.



which has been discussed in a previous communication.

Ionic reactions in which one ionic state passes over into another ionic state can be treated in the same way. Examples treated in detail³ are substitutions of the kind



An expansion of this work is given in the present issue of these *Transactions* by one of the authors.

³ Wigner, *Physic. Rev.*, 1932, 40, 749.

Calculations were carried out at the earliest stage of our work* with respect to the reactions:

(a) Sodium vapour and alkylhalogenides (e.g. $\text{Na} + \text{ClCH}_3 = \text{NaCl} + \text{CH}_3$).

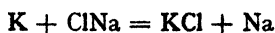
(b) Sodium vapour and the halogens (e.g. $\text{Na} + \text{Cl}_2 = \text{NaCl} + \text{Cl}$).

(c) Alkalimolecules and halogen atoms (e.g. $\text{Na}_2 + \text{Cl}$).

A recent application of the theory has been made by A. G. Evans and M. G. Evans⁴ to the reactions of alkalimetal vapours with hydrogen-halides.

A theorem deduced for ionogenic reactions by the authors connects the heat of reaction with the activation energy in the following way:

It is obvious from Fig. 1 that if we substitute the symmetrical reaction 2 by a reaction of a similar type which is accompanied by a positive heat of reaction, e.g.



the main change will be a *depression* of the surface representing the final state and that this will result in a decrease of the height of the intersection line of the two surfaces, leading to a reduction of the activation energy.

By generalising this argument we arrive at the conclusion that where, in a series of analogous reactions, there is an increase in reaction heat, the activation energy will suffer a parallel decrease.

In Fig. 3

we give a diagrammatic illustration for the case of a series of reactions



with a series of radicals R' R'' R''' introduced for R . We direct our attention exclusively to the influence of the variation of the binding

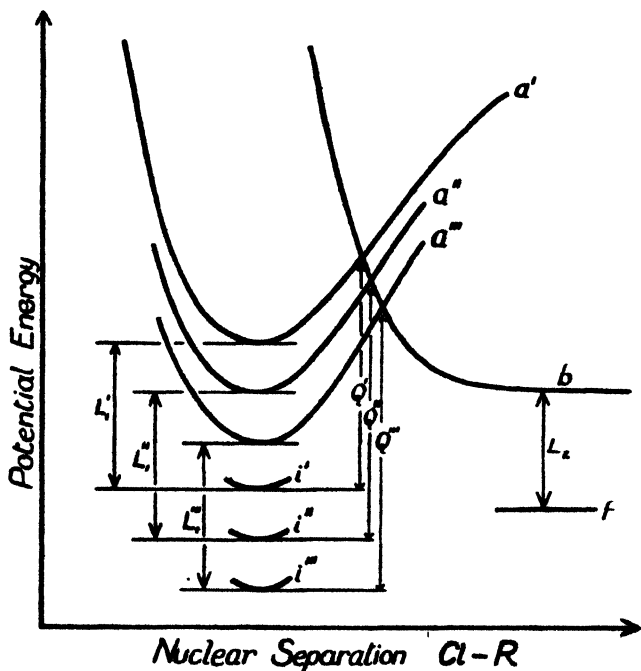


FIG. 3.—The diagram illustrates how for a series of alkyl chlorides R' , R'' , R''' the activation energies Q' , Q'' , Q''' decrease as the heats of reaction increase. (It is assumed that $L_1' = L_1'' = L_1'''$).

* The numerical results are being prepared for publication.

⁴ *Trans. Faraday Soc.* This vol., p. 1400.

energies ClR . Accordingly, we assume that the repulsive curve b remains unchanged and that the energy terms L_1 and L_2 are also influenced to a slight extent only. The activation energies will then be scaled in the same sequence as the heats of reaction, which of course, are determined by the bond strengths. The correctness of this conclusion is demonstrated by the parallelism of reaction velocity with falling frequencies of the $\text{Cl}-\text{R}$ bond, indicating falling bond energies and increasing heats of the reaction $\text{Na} + \text{ClR} = \text{NaCl} + \text{R}$.⁵

In a recent paper the authors⁶ have shown that the strength of secondary $\text{C}-\text{I}$ bond is 3500 Cal. less than that of a primary bond. On the other hand, the activation energy of the reaction (1) is found to be re-

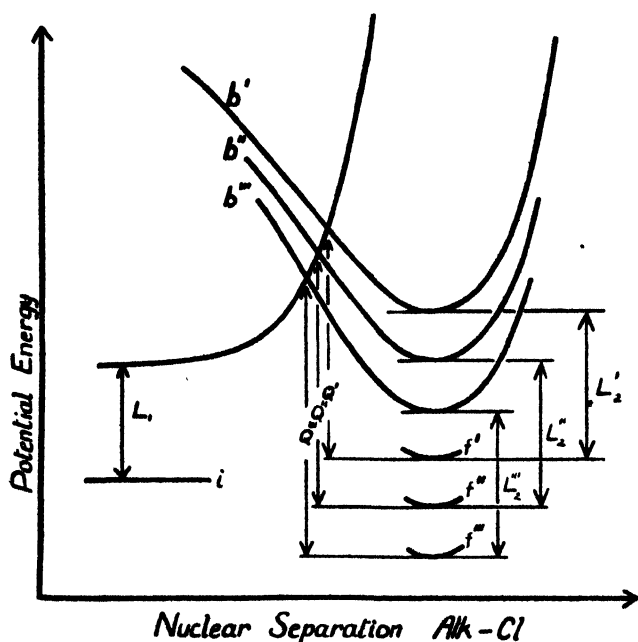


FIG. 4.—The diagram illustrates that when an alkyl chloride reacts with various alkali metals the activation energy should decrease as the heat of reaction increases. (It is assumed that $L_1' = L_1'' = L_2'''$).

tions along a plane $(\text{Cl} \dots \text{R})_{\text{int.}} = \text{const.}$, i.e. a plane section going through the transition state parallel to the $(\text{Alkali} \dots \text{Cl})$ axis, as illustrated in Fig. 4. In this diagram the abscissa follows decreasing values on the $(\text{Alkali} \dots \text{Cl})$ axis, so that we have the initial state of reaction (1) in both Fig. 3 and Fig. 4 on the left, and the final state on the right.

By applying a reasoning analogous to that demonstrated by Fig. 4 we find that the reaction velocities of reaction (1) should increase in the sequence $\text{Na} \rightarrow \text{K} \rightarrow \text{Rb} \rightarrow \text{Cs}$. Some indications of this effect have been found by M. G. Evans and A. G. Evans.⁴ An attempt to test our conclusion more definitely by measuring the reaction rates of various alkali metals with alkyl halides is being made at present in this laboratory.

⁵ W. Heller and M. Polanyi, *Comp. rend.*, 1934, 199, 1118.

⁶ *Trans. Faraday Soc.*, 1935, 31, 482.

⁷ Meer and Polanyi, *Z. physik. Chemis.*, 1932, B 19, 164.

duced by 3000 Cal. if the position of the Cl atom is changed from the primary to the secondary.⁷ This shows that the variations in bond strength are sufficiently large to account for the variability in reaction velocity.

An analogous conclusion may be drawn for the variation of the alkali metal. We have then to consider sec-

Some new illustrations of the validity of the theorem connecting reaction velocity with reaction heat form the subject of a paper given in the present issue by one of the authors.

A new line derived by J. Horiuti in conjunction with one of the authors⁸ has expanded the theory of ionogenic reactions to the various cases of proton transfer. These are: electrolytic dissociation of weak acids; acid-base catalysis; spontaneous ionisation of hydrogen on metal surfaces and electrolytic discharge of H^+ -ions on electrodes; H^+ -ion catalysis of esterhydrolysis. Brønsted's laws of acid-base catalysis and Tafel's equation of overvoltage appear to form special cases of the theorem connecting reaction heat with activation energy.

Lastly, it has been pointed out by M. G. Evans and one of the authors,⁹ that the treatment of ionogenic reactions can be applied to cases in which no ions are formed, but other changes in electronic structure is involved, e.g. $CO + H_2 = H_2CO$.

Diabatic Reactions.

In our theory of ionogenic reactions we have assumed that there is no restriction laid upon the system to pass from one electronic state to another; i.e. the reaction proceeds adiabatically. We must now face this assumption with the fact that diabatic reactions have actually been observed in some cases and that notable authorities have stated that in some of the very cases in which we are concerned, this is the only path the reaction can follow.

Diabatic chemical reactions have been recognised firstly in predissociation by Bonhoffer and L. Farkas¹⁰ and L. Kronig.¹¹ In the well-known energy-diagram of predissociation, two "crossing" levels are present, and the excited molecule is known to go diabatically through the crossing. We will show later that the emission of continuous light accompanying certain chemical reactions (primary chemiluminescence) can be explained as a process representing, roughly speaking, the inverse of predissociation.

Diabatic processes in ordinary (non-photochemical and non-luminescent) chemical reactions have been discussed by Wigner and Pelzer¹² and by F. London.¹³ The former authors have pointed out that the dissociation of N_2O is probably not adiabatic and that, in consequence, the decomposition rate of N_2O is probably restricted by a temperature independent coefficient representing the probability of the diabatic transition.

A fundamental study of diabatic reactions in which the alternative probabilities for diabatic and adiabatic processes were established has been given by F. London¹³ and independently by Landau.¹⁴

F. London based his treatment on an earlier paper of Kallmann and London containing a theory of the energy transfer between two particles. The chemical example given by London is the reaction between a K atom and a Cl atom. His calculation proves that such collisions will invariably lead to the diabatic formation of a homopolar KCl molecule and (primarily) not to the ionic KCl molecule. London extends this

⁸ *Acta Physico Chemica*, U.S.S.R. 1935, 2, 505.

⁹ *Trans. Faraday Soc.*, 1935, 31, 875.

¹⁰ *Z. physik. Chem.*, 1928, 134, 337.

¹¹ *Z. Physik*, 1928, 80, 347; 1930, 62, 300.

¹² *Z. physik. Chem.*, 1932, B 15, 445.

¹³ *Z. Physik*, 1932, 74, 143.

¹⁴ *Physik. Z. Sowjet Union*, 1932, 1, 88; 1932, 2, 46.

result to the reaction $K + Cl_2 = KCl + Cl$ by assuming that the second Cl atom acts merely as a "third body" in a three-body collision.

London's conclusion with respect to the reaction $K + Cl_2 = KCl + Cl$ is contrary to experience. If homopolar KCl were to be primarily formed, such a process would be highly endothermic, since the heat of the reaction $K + Cl_2 = KCl$ (ionic) + Cl is only 40 Kal., whereas the energy level of homopolar KCl lies considerably more than 40 Kal. above the energy of ionic KCl. The discrepancy is explained by reference to our own treatment given above, which makes it obvious that the chemical forces acting between the two Cl atoms, form an essential part of the reaction mechanism which, therefore, cannot be treated as a three-body collision.

A preference for the diabatic process would cause the reaction rate to have an abnormally small temperature independent factor; * it would make the reactions appear abnormally slow when considering their activation energies. None of the cases to which we have applied our theory are of this kind and, therefore, we felt justified in setting aside provisionally, all consideration of diabatic processes.

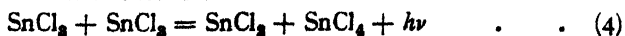
In the light of the theories of London and of Landau, this means that we might assume the perturbation energy W to be not much smaller than kT .

Since in the previous discussion we have assumed that the energy of the transition state is given by the crossing point, it is desirable that the magnitude $\frac{1}{2}W$, by which the energy of the transition state is lowered, should not be too large.

Suppose we aim at a calculation of the activation energy with an accuracy of 10 Kal. (which is all that can be reasonably expected at the moment) then we have to assume that W (while being not much smaller than kT) is not larger than 20 Kal. This leaves a wide range of about 1 : 1000 for the admissible values of W . In a paper, which Mr. M. G. Evans and one of the authors have now in preparation, the value of W will be discussed in detail, and it will be attempted to remove some of the arbitrariness of our assumptions hitherto made with respect to this magnitude. This paper will show that the perturbation energy W is small when there is an "electron switch" involved in the reaction.

Primary Chemiluminescence.

When sodium vapour reacts with $SnCl_4$ a brilliant luminescence is observed, which shows a completely continuous spectrum.¹⁵ It has been pointed out in the paper communicating this observation that this light cannot be produced in the way in which other previously known chemiluminescences are known to arise. Those luminescences are to be explained by a molecule formed in the primary process colliding with and exciting a neighbouring atom, *e.g.* the luminescence of the sodium vapour and chlorine arises by the collision of an NaCl-molecule, formed in the reaction $Na_2 + Cl$ colliding with a neighbouring Na-atom. The light of the $(Na - SnCl_3)$ -luminescence cannot be of this kind; it has to be of a "primary" character, *i.e.* to be emitted not after, but during the chemical process. The most probable explanation is that the $SnCl_3$ radicals formed by the reaction $Na + SnCl_4 = NaCl + SnCl_3$, lead to a subsequent luminescent reaction:



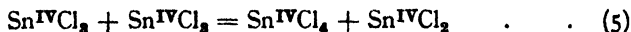
* Supposing that no primary chemiluminescence occurs (*vide infra*).

¹⁵ G. Schay and M. Polanyi, *Z. Physik*, 1928, 47, 814.

By expanding our theory of ionogenic reactions a mechanism can be suggested for the emission of continuous light in conjunction with a reaction of the above type.

The reaction involves an electronic rearrangement of a Sn-atom from the quadrivalent to the divalent state, analogous to the transition of a particle from an atomic to an ionic state. We can depict the reaction as a transfer of a Cl-atom from one quadrivalent Sn-atom to another quadrivalent Sn-atom, accompanied by a transition of the former Sn-atom into the divalent state. We can then restrict ourselves to the consideration of these three particles, Sn, Cl and Sn and we can construct two energy surfaces corresponding to the two states of these particles, namely the surface ($\text{Sn}^{\text{IV}} \dots \text{Cl} \dots \text{Sn}^{\text{IV}}$) and the surface ($\text{Sn}^{\text{IV}} \dots \text{Cl} \dots \text{Sn}^{\text{II}}$). The initial state of the reaction (4) lies on the former surface, its final state on the latter. There is also a spurious "initial state" on the surface ($\text{Sn}^{\text{IV}} \dots \text{Cl} \dots \text{Sn}^{\text{II}}$) and also a "final state" (which we have likewise considered as spurious in the analogous cases treated above) on the ($\text{Sn}^{\text{IV}} \dots \text{Cl} \dots \text{Sn}^{\text{IV}}$) surface.

Our attention is directed to the "final state" of the ($\text{Sn}^{\text{IV}} \dots \text{Cl} \dots \text{Sn}^{\text{IV}}$) surface. It lies much higher than the stable final state ($\text{Sn}^{\text{IV}} \dots \text{Cl} \dots \text{Sn}^{\text{II}}$). But it can be shown that it does not lie so high as to cause the reaction



to be endothermic. The heat of 70 Kal. produced in reaction (4) is the equivalent of the difference in bond strength of the third Cl atom of $\text{Sn}^{\text{IV}}\text{Cl}_3$ and the fourth Cl atom in $\text{Sn}^{\text{IV}}\text{Cl}_4$. Supposing both molecules were to be strictly homopolar, we could adopt the argument which Mecke¹⁰ applied to the difference in the strengths of the third and fourth C—H bonds in CH_4 . We would consider that the two homopolar bond energies E_1 and E_2 as defined by the equations

$$\begin{aligned}\text{Sn}^{\text{IV}}\text{Cl}_4 &= \text{Sn}^{\text{IV}}\text{Cl}_3 + \text{Cl} - E_1 \\ \text{Sn}^{\text{IV}}\text{Cl}_3 &= \text{Sn}^{\text{IV}}\text{Cl}_2 + \text{Cl} - E_2\end{aligned}$$

should be equal, i.e. $E_1 = E_2$ and that in consequence reaction (5) should be thermoneutral.

Actually, in both $\text{Sn}^{\text{IV}}\text{Cl}_4$ and $\text{Sn}^{\text{IV}}\text{Cl}_3$ a considerable part of the bond energy is of a polar nature. The polar term should be larger in E_1 than in E_2 , since it increases with the charge of the metallic nucleus. In consequence (assuming once more that the homopolar terms in E_1 and in E_2 are equal) we conclude $E_1 > E_2$, i.e. reaction (5) to be exothermic.

There is, therefore, in this case, no difficulty with respect to reaction heat for the process to proceed adiabatically, i.e. according to reaction (5). Assuming this to be the case, there is a primary formation of an $\text{Sn}^{\text{IV}}\text{Cl}_2$ molecule, which can pass over by an electronic transition accompanied by emission of light, into the stable $\text{Sn}^{\text{II}}\text{Cl}_2$ state. To account for the continuous character of the light we must assume that the emission occurs while the newly formed molecule is still in contact with the newly formed SnCl_4 molecule, variable quantities of energy being taken up by the translation motion of the two newly formed molecules flying off in opposite directions. The assumption of such a process appears justifiable, since it represents an exact inversion of the predissociation process.

¹⁰ *Z. physik. Chemie*, 1930, B 7, 108.

A diagrammatic sketch of this theory is given in Fig. 5 in which a section of the two energy surfaces is given along the "reaction path." * The figure is so designed as to show the fact that the reaction has no noticeable activation energy. The arrows indicate the transitions which give rise to emission of light.

More recently, a number of chemiluminences have been observed ¹⁷ when sodium vapour is brought into reaction with polyhalides of the fourth and fifth groups of the periodic system. All these appear to be of the character of the $(\text{Na} - \text{SnCl}_4)$ luminescence. Since all the polyhalides in question show a variability of valency in their halogen com-

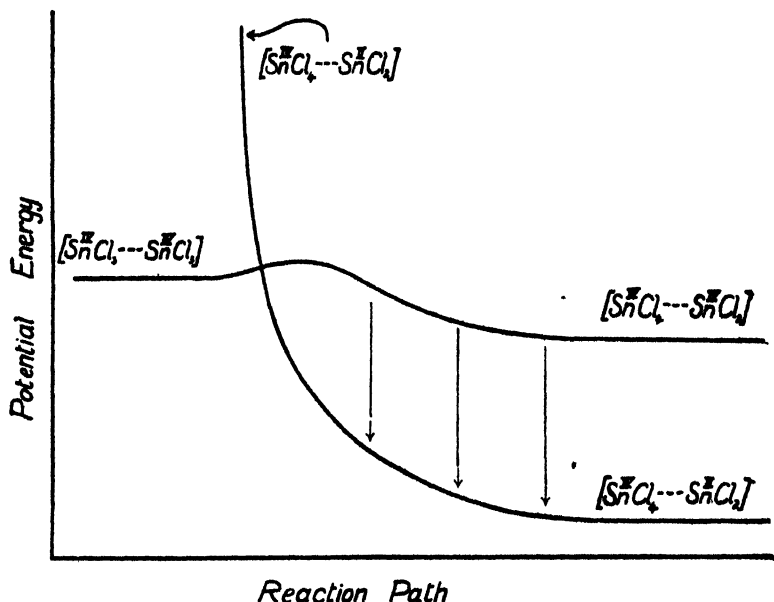


FIG. 5.

pounds, there seems no difficulty in extending our explanation to these new cases.

Actually, the present theory seems to be the only explanation offering itself for continuous spectra emitted in a gas reaction.

Summary.

An outline of the theory of ionogenic reactions and a list of its applications is given with special reference to the theorem connecting reaction, heat and reaction velocity. It is shown how this work is related to previous considerations of diabatic reactions.

The primary chemiluminescence is described as an inverse process of predissociation involving diabatic chemical reactions immediately followed by the emission of light.

* We imagine a surface to be erected vertically to the $(\text{Sn} \dots \text{Cl}) - (\text{Cl} \dots \text{Sn})$ -plane, and following the reaction path.

¹⁷ W. Heller and M. Polanyi, *Comp. rend.*, 1934, 199, 1118.

MECHANISM OF IONIC REACTIONS. THE HEAT OF IONIC SUBSTITUTION REACTIONS.

By R. A. OGG, JR.

Received 4th July, 1935.

In previous communications ¹ with M. Polanyi the author has discussed the mechanism of exchange reactions between negative ions and homopolar molecules. The validity of the conclusions arrived at was tested in the case of a certain group of simple reactions, *i.e.*, exchange reactions between halide ions and alkyl halides, by calculating the theoretical activation energies to be expected and comparing these with experiment. It is desired here to consider various other cases of exchange reactions of negative ions in light of the theoretical considerations previously advanced. For the reactions here treated it does not appear feasible to attempt the calculation of the absolute values to be expected for the activation energy, since the various approximations necessary even for the simple case of an alkyl halide and halide ion involve far too serious an uncertainty when more complicated systems are considered. We shall therefore restrict ourselves chiefly to illustration (on the basis of essentially experimental evidence) of the following theorem, which was deduced in the previous communication. Let the compound XY be substituted by different negative ions Z_1^- , Z_2^- , Z_3^- . If the repulsive potential between the negative ion and X does not vary greatly in the series, while the reactions are increasingly more exothermic in the order named, then the respective activation energies *decrease* in this order. As a consequence of this theorem it may be said in general that ionic interchange reactions having large positive heats of reaction are characterised by moderately small energies of activation. The experimental facts are found to be in agreement with this corollary, in so far as all interchange reactions involving negative ions other than halide ions, and known to occur with appreciable velocities under ordinary conditions, can be shown to be considerably exothermic.

Estimation of Reaction Heats of Ionic Interchange Reactions.

It is found that the greater part of the evidence which we shall consider relates to reactions between alkyl halides and various negative ions such as OH^- , OCH_3^- , SH^- , CN^- , etc. In no case does there appear to be very reliable direct evidence as to the heats of reaction, and in consequence we are compelled to estimate these indirectly, using the necessary intermediate reactions and applying Hess' Law.

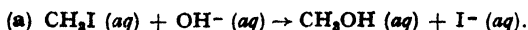
The necessary data for the heat effect of the various individual steps may be derived in large part from standard sources. Deficiency of data with regard to heats of mixing of liquids necessitates an assumption which is made throughout the calculations given below. The heat of evaporation of an organic substance (such as an alkyl halide) from solution in a polar solvent (such as water) is taken to be equal to the heat of vaporisation of

¹ R. A. Ogg, Jr. and M. Polanyi, *Proc. Manch. Lit. Phil. Soc.*, 1934, **78**, 41; *Trans. Faraday Soc.*, 1935, **31**, 604.

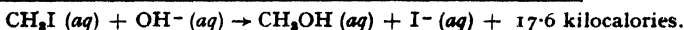
the pure organic liquid, *i.e.*, the heat of mixing of the pure liquid with the solvent is neglected. The resulting inaccuracy is in most cases small, and since the difference of two such heats of evaporation enters into the value of the overall reaction heat, the error may justifiably be neglected.

As examples of the calculations, we shall give the details of estimating the heats of reaction for several ionic interchange reactions. The first example chosen is the reaction of methyl iodide with hydroxyl ion in aqueous solution. The respective reaction heats are in kilo-calories per mole, and refer to approximately room temperature.

The most serious uncertainties arise in the heat effect of steps (3) and



1. $\text{CH}_3\text{I} (aq) \rightarrow \text{CH}_3\text{I} (l)$	0.0 ^a
2. $\text{CH}_3\text{I} (l) \rightarrow \text{CH}_3\text{I} (g)$	-6.5 ^a
3. $\text{CH}_3\text{I} (g) \rightarrow \text{CH}_3 (g) + \text{I} (g)$	-45.0 ^a
4. $\text{CH}_3\text{OH} (l) \rightarrow \text{CH}_3\text{OH} (aq)$	0.0 ^a
5. $\text{CH}_3\text{OH} (g) \rightarrow \text{CH}_3\text{OH} (l)$	+8.6 ^a
6. $\text{CH}_3 (g) + \text{OH} (g) \rightarrow \text{CH}_3\text{OH} (g)$	+76.0 ^a
7. $\text{H} (g) + \text{I} (g) \rightarrow \text{HI} (g)$	+70.9 ^a
8. $\text{HI} (g) \rightarrow \text{HI} (aq)$	+19.5 ^a
9. $\text{HI} (aq) \rightarrow \text{H}^+(aq) + \text{I}^- (aq)$	0.0 ^b
10. $\text{H}_2\text{O} (g) \rightarrow \text{H} (g) + \text{OH} (g)$	-110.0 ^a
11. $\text{H}_2\text{O} (l) \rightarrow \text{H}_2\text{O} (g)$	-9.7 ^a
12. $\text{H}^+(aq) + \text{OH}^- (aq) \rightarrow \text{H}_2\text{O} (l)$	+13.8 ^b



(6), *i.e.*, in the energies of the corresponding organic linkages. These have been derived from heats of combustion on the assumption of the additivity of bond energies. Any systematic error from this assumption is eliminated by the fact that the difference of two bond energies enters into the value of the overall reaction heat. However, the probable errors in the heats of combustion still remain, and are presumably of the order of one or two kilocalories per mole. The heat effects of the various other steps are known with considerable accuracy. It appears probable that the value of the overall reaction heat is trustworthy to within some two or three kilocalories per mole.

It appears that the value estimated for the heat of the above reaction would not be greatly altered were a different solvent, say ethyl alcohol, to be employed. The chief effect of a change of solvent would be on the heat effect of steps (8) and (12), and even for these a difference of more than a few kilocalories per mole is hardly to be expected.

Likewise, it appears that the estimated value should apply essentially to reactions of other alkyl iodides with hydroxyl ion. Differences caused by the substitution of a larger alkyl radical for methyl, as increase in heats of vaporisation, decrease in bond energies, etc., should cancel systematically, leaving only small second order effects on the final value of reaction heat.

The above example is typical of the majority of reactions which we shall consider. These are mostly interchange reactions of alkyl halides with the anions of weak acids (*i.e.*, of water in the example given). Hence replacement in the above list of steps (4), (5), (6), (10), (11) and (12) by those appropriate for the particular weak acid in question is all that is necessary for estimate of the heat effect in the reaction of an alkyl iodide with a basic negative ion. The changes to be made for other alkyl halides are obvious.

^a By the assumption with regard to heats of mixing of liquids.

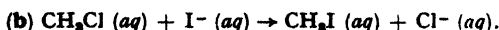
^b Landolt-Börnstein Tabellen.

^c N. V. Sidgwick, "The Covalent Bond in Chemistry." George Fisher Baker Lectures, Cornell University (1932).

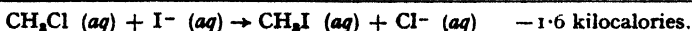
^d The heat of dissociation of strong electrolytes is taken as zero.

A consideration of great importance (*vide infra*) relates to reactions of a given alkyl halide with a series of basic anions derived from acids having a common atom linked to the acidic hydrogen. Such a series is CH_3COO^- , $\text{C}_6\text{H}_5\text{O}^-$, HO^- , these ions being derived from acids with an oxygen-hydrogen linkage. The step corresponding to (6) in the above example should have practically the same heat effect for each reaction of the series, since the same organic linkage is broken in each case (constitutive influence on the binding energy may be regarded as of secondary importance). The same applies essentially to the step corresponding to (10), although the constancy of bond energy is not as rigorous here (the greatest difference appears between the heats of dissociation of water and of organic oxygen-hydrogen links, the respective values of which are 110.0 and 106.0 kilocalories per mole). Further, the respective heat effects of (5) and (11) will not vary greatly in the series, since the heats of evaporation are at most rather small. It is only for the step corresponding to (12), *i.e.*, for the ionisation of the weak acid, that the heat effect will vary considerably in this series. Hence in such a series the order of the respective overall reaction heats will be determined by the order of the heats of ionic dissociation of the corresponding weak acids. The weaker the acid, *i.e.*, the greater its heat of dissociation, the more exothermic will be the reaction of its anion with a given alkyl halide.

A less common, but still important type of reaction involves the interchange of the anion of a strong acid with an alkyl halide. While the treatment of such a case does not differ greatly from that already considered, we shall give as an example the estimation of the heat of reaction of methyl chloride with iodide ion in aqueous solution.



1. $\text{CH}_3\text{Cl} (aq) \rightarrow \text{CH}_3\text{Cl} (l)$	0.0 ²
2. $\text{CH}_3\text{Cl} (l) \rightarrow \text{CH}_3\text{Cl} (g)$	-5.5 ³
3. $\text{CH}_3\text{Cl} (g) \rightarrow \text{CH}_3 (g) + \text{Cl} (g)$	-75.0 ⁴
4. $\text{CH}_3\text{I} (l) \rightarrow \text{CH}_3\text{I} (aq)$	0.0 ³
5. $\text{CH}_3\text{I} (g) \rightarrow \text{CH}_3\text{I} (l)$	+6.5 ³
6. $\text{CH}_3 (g) + \text{I} (g) \rightarrow \text{CH}_3\text{I} (g)$	+45.0 ⁴
7. $\text{H} (g) + \text{Cl} (g) \rightarrow \text{HCl} (g)$	+102.2 ⁴
8. $\text{HCl} (g) \rightarrow \text{HCl} (aq)$	+17.6 ³
9. $\text{HCl} (aq) \rightarrow \text{H}^+ (aq) + \text{Cl}^- (aq)$	0.0 ⁵
10. $\text{HI} (g) \rightarrow \text{H} (g) + \text{I} (g)$	-70.9 ⁴
11. $\text{HI} (aq) \rightarrow \text{HI} (g)$	-19.5 ³
12. $\text{H}^+ (aq) + \text{I}^- (aq) \rightarrow \text{HI} (aq)$	0.0 ⁵

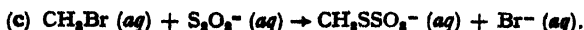


This reaction is thus seen to have a practically negligible heat effect in aqueous solution, and considerations similar to those already advanced would lead one to infer that the heat effect will be likewise very small in any polar solvent.

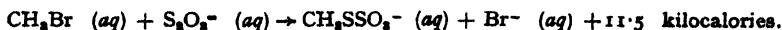
To estimate the heat effect of reactions of this type it is necessary to know the heat of transfer of the corresponding strong acid from the gaseous state to the solvent considered.

A third type of reaction which we shall consider is between an alkyl halide and bivalent negative ion. As an example, the heat of reaction of methyl bromide with thiosulphate ion may be estimated by a method essentially similar to the above, but involving some necessary modifications.

In the following calculation some assumptions appear which require explanation. Thus it is assumed that the heats of hydration of the ions $\text{CH}_3\text{SSO}_3^-$ and HSSO_3^- are identical, and hence that steps (4) and (10) have the same heat effect. It is to be noted that (5) implies the rupture of a carbon-sulphur linkage; and (9) that of a hydrogen-sulphur linkage. Thiosulphuric acid appears to be a strong (although unstable) electrolyte in water—hence the zero heat effect for (11).



1. $\text{CH}_3\text{Br} (aq) \rightarrow \text{CH}_3\text{Br} (l)$	0.0 [*]
2. $\text{CH}_3\text{Br} (l) \rightarrow \text{CH}_3\text{Br} (g)$	-7.0 [*]
3. $\text{CH}_3\text{Br} (g) \rightarrow \text{CH}_3 (g) + \text{Br} (g)$	-62.0 [*]
4. $\text{CH}_3\text{SSO}_3^- (g) \rightarrow \text{CH}_3\text{SSO}_3^- (aq)$	+S [*]
5. $\text{CH}_3 (g) + \text{SSO}_3^- (g) \rightarrow \text{CH}_3\text{SSO}_3^- (g)$	+62.0 [*]
6. $\text{H} (g) + \text{Br} (g) \rightarrow \text{HBr} (g)$	+86.7 [*]
7. $\text{HBr} (g) \rightarrow \text{HBr} (aq)$	+20.0 [*]
8. $\text{HBr} (aq) \rightarrow \text{H}^+ (aq) + \text{Br}^- (aq)$	0.0 [*]
9. $\text{HSSO}_3^- (g) \rightarrow \text{H} (g) + \text{SSO}_3^- (g)$	-88.2 [*]
10. $\text{HSSO}_3^- (aq) \rightarrow \text{HSSO}_3^- (g)$	-S [*]
11. $\text{H}^+ (aq) + \text{S}_2\text{O}_8^{2-} (aq) \rightarrow \text{HSSO}_3^- (aq)$	0.0 [*]



The above methods have been used to estimate the heat effect of a large number of ionic reactions involving methyl chloride, bromide and iodide. Reactions of methyl fluoride have not been considered, not only because of deficiencies in thermal data relating to fluorine compounds, but also because of the scantiness of experimental evidence relating to such reactions. The calculated heats of reaction are given in Table I., together with the corresponding experimental activation energies. In the majority of cases these activation energies have not been directly observed, but are roughly estimated from the approximate reaction velocity at some known temperature, assuming the bimolecular constant to be given by the expression $2.8 \times 10^{11} e^{-Q/RT}$ (mole/litre)⁻¹ sec.⁻¹.⁷ Such estimated values are enclosed in parentheses.

In many cases only the approximate magnitude of the velocity is known. For such cases the corresponding activation energies are enclosed in parentheses and starred. The accuracy of such values is, of course, low. Many of the observed activation energies refer to reactions involving an alkyl halide other than methyl. However, for reasons previously discussed, it is believed that constitutive influences on the reaction heat are relatively small, and hence comparison with the calculated results for methyl halides is justified. Likewise, it is believed that the particular polar solvent used will not change the values greatly.

The required thermal data for estimating the heat effects have all been drawn from the sources previously cited.^{3,4} The values refer to approximately 20° C.

While the list of reactions given is not exhaustive, it embraces the majority of important examples. There are, of course, many obvious extensions of the list. Thus the estimated heat effects for reactions of alkyl halides with ethylate ion will be almost exactly the same as for the corresponding reactions with methylate ion, since the heats of ionisation of methyl and ethyl alcohols are nearly identical. Likewise, reactions of substituted phenolate ion will have heat effects differing but little from those of phenolate ions. The data for reactions of acetate ion are representative of those for reactions of ions derived from weak acids with nearly the same heat of ionisation as acetic acid—such as benzoic and paratoluenesulphonic acids. A few important reaction types are missing from the list, due to deficiencies in the necessary thermal data. (Notable among these are the reactions with thiocyanate ion.) However, even in these cases qualitative evidence, such as the degree of completeness of the reactions, indicates them to be definitely exothermic.

* S is the unknown heat of solution of the gaseous ion in water.

⁷ E. A. Moelwyn-Hughes, *The Kinetics of Reactions in Solution*, Oxford, 1933.

TABLE I.

No.	Reaction.	Solvent.	<i>H</i> kilocalories per mole.	Experimental Activation Energy, kilocalories/mole.
1	$\text{CH}_3\text{Cl} + \text{I}^-$	H_2O	- 1.6	23.5 in $(\text{CH}_3)_3\text{CO}^*$
2	$\text{CH}_3\text{Br} + \text{I}^-$	H_2O	- 1.2	(19) in $(\text{CH}_3)_3\text{CO}^{10}$
3	$\text{CH}_3\text{Cl} + \text{Br}^-$	H_2O	- 0.4	(20) in H_2O^{11}
4	$\text{CH}_3\text{Cl} + \text{HO}^-$	H_2O	+ 18.0	23 in $\text{C}_2\text{H}_5\text{OH}^{12}$
5	$\text{CH}_3\text{Br} + \text{HO}^-$	H_2O	+ 16.4	21 in $\text{C}_2\text{H}_5\text{OH}^{12}$
6	$\text{CH}_3\text{I} + \text{HO}^-$	H_2O	+ 17.6	21 in $\text{C}_2\text{H}_5\text{OH}^{12}$
7	$\text{CH}_3\text{Cl} + \text{C}_2\text{H}_5\text{O}^-$	$\text{C}_2\text{H}_5\text{OH}$	+ 17.1 ⁸	21 in $\text{C}_2\text{H}_5\text{OH}^{20}$
8	$\text{CH}_3\text{Br} + \text{C}_2\text{H}_5\text{O}^-$	$\text{C}_2\text{H}_5\text{OH}$	+ 15.5 ⁸	21 in $\text{C}_2\text{H}_5\text{OH}^{20}$
9	$\text{CH}_3\text{I} + \text{C}_2\text{H}_5\text{O}^-$	$\text{C}_2\text{H}_5\text{OH}$	+ 16.7 ⁸	19.5 in $\text{C}_2\text{H}_5\text{OH}^{12}$
10	$\text{CH}_3\text{Cl} + \text{C}_2\text{H}_5\text{O}^-$	H_2O	+ 13.4	19.5 in $\text{C}_2\text{H}_5\text{OH}^{20}$
11	$\text{CH}_3\text{Br} + \text{C}_2\text{H}_5\text{O}^-$	H_2O	+ 11.8	19.5 in $\text{C}_2\text{H}_5\text{OH}^{20}$
12	$\text{CH}_3\text{I} + \text{C}_2\text{H}_5\text{O}^-$	H_2O	+ 13.0	22.3 in $\text{C}_2\text{H}_5\text{OH}^{14}$
13	$\text{CH}_3\text{Cl} + \text{CH}_3\text{COO}^-$	H_2O	+ 10.2	22.3 in $\text{C}_2\text{H}_5\text{OH}^{20}$
14	$\text{CH}_3\text{Br} + \text{CH}_3\text{COO}^-$	H_2O	+ 8.6	(28)* in $\text{CH}_3\text{COOH}^{15}$
15	$\text{CH}_3\text{I} + \text{CH}_3\text{COO}^-$	H_2O	+ 9.8	(28)* in $\text{CH}_3\text{COOH}^{20}$
16	$\text{CH}_3\text{Cl} + \text{HS}^-$	H_2O	+ 19.7	(28)* in $\text{CH}_3\text{COOH}^{20}$
17	$\text{CH}_3\text{Br} + \text{HS}^-$	H_2O	+ 18.1	(28)* in $\text{CH}_3\text{COOH}^{20}$
18	$\text{CH}_3\text{I} + \text{HS}^-$	H_2O	+ 19.3	(22)* in $\text{C}_2\text{H}_5\text{OH}^{18}$
19	$\text{CH}_3\text{Cl} + \text{CN}^-$	H_2O	+ 19.8	(22)* in $\text{C}_2\text{H}_5\text{OH}^{20}$
20	$\text{CH}_3\text{Br} + \text{CN}^-$	H_2O	+ 18.2	(22)* in $\text{C}_2\text{H}_5\text{OH}^{20}$
21	$\text{CH}_3\text{I} + \text{CN}^-$	H_2O	+ 19.4	(29)* in $\text{C}_2\text{H}_5\text{OH}^{17}$
22	$\text{CH}_3\text{Cl} + \text{S}_2\text{O}_3^{2-}$	H_2O	+ 13.1	19.9 in H_2O^{18}
23	$\text{CH}_3\text{Br} + \text{S}_2\text{O}_3^{2-}$	H_2O	+ 11.5	19.4 in H_2O^{18}
24	$\text{CH}_3\text{I} + \text{S}_2\text{O}_3^{2-}$	H_2O	+ 12.7	18.8 in H_2O^{18}
25	$\text{CH}_3\text{Cl} + \text{SO}_3^{2-}$	H_2O	+ 9.6	(17.9) in H_2O^{19}
26	$\text{CH}_3\text{Br} + \text{SO}_3^{2-}$	H_2O	+ 8.0	(15.3) in H_2O^{19}
27	$\text{CH}_3\text{I} + \text{SO}_3^{2-}$	H_2O	+ 9.2	(14.9) in H_2O^{19}

Discussion.

It is seen that the results in Table I. are in definite substantiation of the corollary stated at the outset, since all of the reactions of the alkyl halides with negative ions other than halide ions are considerably exothermic. The very small heat effects for the reactions with halide ions justify the assumption made in the previous communication¹ that such substitutions have a zero heat of reaction.

The validity of the theorem stated at the outset is seen to be confirmed by the data in Table I. referring to the reactions involving HO^- , $\text{C}_2\text{H}_5\text{O}^-$,

¹ It is assumed that the heats of solution of hydrogen halides in $\text{C}_2\text{H}_5\text{OH}$ is the same as in H_2O .

² J. B. Conant and R. E. Hussey, *J. Amer. Chem. Soc.*, 1925, 47, 476.

¹⁰ A. Szabo, *Dissertation*, Berlin, 1933.

¹¹ A. R. Olson and F. A. Long, *J. Amer. Chem. Soc.*, 1934, 56, 1294.

¹² G. H. Grant and C. N. Hinshelwood, *J. Chem. Soc.*, 1933, 258.

¹³ W. Hecht and M. Conrad, *Z. physikal. Chem.*, 1889, 3, 450.

¹⁴ D. Segaller, *J. Chem. Soc.*, 1914, 105, 106.

¹⁵ B. M. Mereshkowsky, *Ann. Chemie*, 1923, 431, 231.

¹⁶ J. Houben, *Methoden der Organischen Chemie*, Berlin, Edition 3, 1930.

¹⁷ A. Lieben and A. Rossi, *Ann. Chemie*, 1871, 159, 58.

¹⁸ A. Slatore, *J. Chem. Soc.*, 1904, 85, 1286.

¹⁹ H. J. Backer and W. A. van Mels, *Rec. trav. chim.*, 1930, 49, 177.

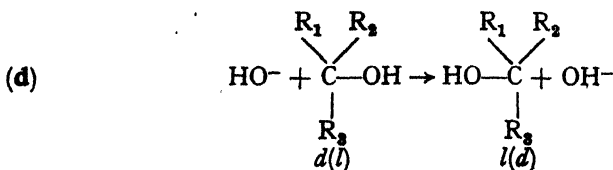
²⁰ In the absence of complete data referring to all three alkyl halides it may be assumed that the usual increase in reaction velocity (*i.e.* decrease in activation energy) in the series chloride, bromide, iodide obtains.

$C_6H_5O^-$ and CH_3COO^- ions. For these reactions, each of which involves the formation of a carbon-oxygen linkage, increasing reaction heat is seen to be accompanied by decreasing activation energy, except for the reactions of hydroxyl and ethylate ions, where the order is reversed. However, the difference between the values for hydroxyl and ethylate ions is less than the estimated uncertainty of the quantities, and that for ethylate ion is subject to an even further uncertainty by a special assumption necessitated.⁸ Therefore the calculated order might easily be reversed for this pair of reactions. When it is considered that the experimental activation energies differ by very little, the agreement is sufficiently satisfactory, and one may consider the theorem as verified.

The series of negative ions Br^- , CH_3COO^- , $C_6H_5O^-$, $C_2H_5O^-$, which was quoted in the previous communication as being, according to Ingold, increasingly active as substituting agents, corresponding to increasing nucleophyllic strength, is seen from Table I. to be a series for which the corresponding substitutions with alkyl halides are arranged in the order of increasing heat effect. The essential reason was discussed following example (a) above, where it was shown that the heat of reaction of a negative ion with hydrogen ion (corresponding to its nucleophyllic strength) is additive in increasing the heat of a substitution reaction by this ion. Hence, if other factors are constant, the heat effects and hence the velocities of substitution reactions of a series of negative ions is in the order of nucleophyllic strength of these ions.

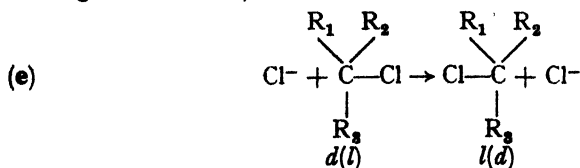
It is to be noticed that for reaction with a given negative ion the calculated heat effects in Table I. are nearly identical for methyl chloride, bromide and iodide. This of course follows from the very small heat effects accompanying the interchange reactions of halide ions with alkyl halides. Hence on the basis of heat effects there is no significant difference between reactions of the different halides. The well-known increase in velocity of reaction with a given negative ion (*i.e.*, decrease in activation energy) in the series chloride, bromide, and iodide is to be explained by the operation of the factors previously considered¹ in causing a similar velocity increase in the series of identical substitutions $Cl^- + CH_3Cl$, $Br^- + CH_3Br$, $I^- + CH_3I$.

Several interesting deductions can be drawn from the data in Table I. Thus it is to be observed that despite the widely differing heat effects of the various reactions, the respective activation energies do not vary greatly. Thus for substitution of methyl chloride by iodide ion and hydroxyl ion respectively, the activation energies differ by only a few kilocalories per mole, although the former reaction is nearly thermo-neutral, while the latter exothermic by some eighteen kilocalories per mole. It therefore appears that the approach of a hydroxyl ion to a saturated carbon atom is attended by considerably greater repulsion than is that of a halide ion. Hence it is to be expected that an "identical substitution reaction" involving hydroxyl ion, as



where there is no reaction heat to contend against the repulsive energy and aid the approach of the hydroxyl ion, would require considerably

greater activation energy than would the corresponding reaction involving a halide ion, as

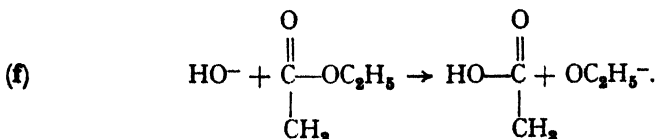


However, in the previous communication it was shown that the expected activation energy for (e) is so large that such a reaction should not be detectable except in certain special cases—in agreement with experimental evidence. Hence one should expect the activation energy of (d) to be so large as to exclude its occurrence under any conditions practically attainable.

In a note²¹ L. Werner, M. Polanyi and the author claimed to have found a measurable rate for reaction (d) in the case of optically active methyl phenyl carbinol. However, subsequent experiments have shown that the loss in optical activity which was first observed on heating the active carbinol with dilute alcoholic potassium hydroxide in sealed tubes at 80° C. was in reality caused by the oxidation of the carbinol (by the oxygen of the enclosed air), presumably to acetophenone. When air was excluded, no loss in optical activity was detectable after heating solutions of the active carbinol in 0.2 *N* alcoholic potassium hydroxide for some twenty-four hours at 150° C. Solutions of the carbinol in approximately 0.5 *N* potassium hydroxide in ethylene glycol were heated at 240° C. in the absence of air for twenty-four hours with no measurable decrease in rotation. The failure to obtain any racemisation under these extreme conditions indicates an activation energy for reaction (d) in this case of at least some forty kilocalories per mole. This experimental result is in agreement with the above conclusion.

Similarly, since all of the reactions in Table I. are considerably exothermic, except for (1), (2) and (3) (involving halide ions) it appears that for each of the various ions considered the identical substitution reaction analogous to (d) will have an activation energy greater than that of (e). It is therefore to be expected that the corresponding racemisations will not be observed under conditions ordinarily attainable. There appears to be no experimental evidence for any such racemisation reaction except in the case of alkyl halides and halide ions.

It has been shown²² that the alkaline hydrolysis of esters is a substitution reaction of hydroxyl ion, as for example



From the principles used in estimating the values in Table I. it is easy to see that (f) should have a nearly negligible heat effect. In fact, (f) is very similar to the identical substitution reaction (d), since the hydroxyl and alkoxyl ions do not differ greatly in nucleophilic strength.

²¹ R. A. Ogg, M. Polanyi and L. Werner, *Chemistry and Industry*, 1934, 53, 614.

²² M. Polanyi and A. L. Szabo, *Trans. Faraday Soc.*, 1934, 30, 508.

Hence, from the foregoing discussion one might expect (f) to have a very large activation energy. Actually, the activation energy for reactions of this type is much smaller than for any of the other reactions considered—of the order of eleven kilocalories per mole.⁷ This great discrepancy is to be attributed to the fact that an acyl carbon atom is being substituted in (f). It is very probable that the single carbon-oxygen linkages are much weaker in such a case than those in an alcohol, and hence that a much decreased activation energy results.¹

In conclusion it may be stated that the experimental evidence regarding the activation energies of practically all substitution reactions of negative ions at a saturated carbon atom has been shown to be in accord with the mechanism proposed for such reactions, and hence that the validity of this mechanism may be considered reasonably well established.

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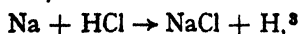
THE RATES OF REACTION OF SODIUM ATOMS WITH HYDROGEN AND DEUTERIUM CHLORIDES.

By C. E. H. BAWN and A. G. EVANS.

Received 5th July, 1935.

Comparison of analogous reactions of hydrogen and deuterium compounds, has shown the existence of marked kinetic differences. These differences arise from two factors dependent on mass: firstly, the reduced collision number of the heavier isotopic molecule; and secondly, the difference in activation energies due to the difference in zero point energies of the reacting molecules. The former factor which is inversely proportional to the square root of the reduced mass of the colliding pair¹ will be small for bimolecular reactions of simple hydrogen or deuterium compounds of appreciable molecular weight with heavy elements or molecules, *e.g.*, the reaction under investigation. In such cases any large differences in the observed reaction velocities of the isotopic molecules must result from a difference in the activation energy. The predominant influence of this factor, has already been demonstrated in several instances, for example, in the reactions of halogen atoms with hydrogen and deuterium molecules.²

The present investigations which are designed to elucidate the mechanism of the reaction,



¹ Eyring, *J. Chem. Physics*, 1935, 3, 111, has recently shown that this factor in certain cases will be $m^{\frac{1}{2}}$ rather than $m^{\frac{1}{2}}$.

² Bonhoeffer, Back and Fajans, *Z. physikal. Chem.*, 1934, B; Back, Bonhoeffer and Moelwyn-Hughes, *Z. physikal. Chem.*, 1934, 27B, 71; Farkas and Farkas, *Naturwiss.*, 1934, 14, 218.

³ This reaction has previously been studied by Schay (*Z. physik. Chem.*, B, 1930, 11, 291) by the method of highly attenuated flame, and by Hartel (*Z. physik. Chem.*, B, 1930, 11, 316) by the diffusion flame method.

have been used to test the above theory and to examine the influence of zero point energy on the rates of reaction. We have found that although the zero point energies of the molecules hydrogen chloride and deuterium chloride in the initial state differ by 1200 Cals. that the reaction of sodium atoms with both HCl and DCl molecules proceed at approximately the same rate. A satisfactory explanation of this result can be provided by a consideration of the "zero point energies in the activated state."

In previous papers ⁴ it has been shown that the reaction takes place by the passage of the reacting system over an energy barrier, the height of which measures the activation energy. A system moving on such a surface will have its energy quantised and at the top of the barrier (transition state) the reaction complex will have all the properties of a normal chemical compound, except in one degree of freedom—that which leads to decomposition. The transition complex will have 3 degrees of rotational freedom, 3 of translational degrees of freedom, and $3N - 7$ characteristic vibrations, and we are thus justified in attributing to it a zero point energy. Furthermore, the deuterium complex will have a lower zero point energy in the transition state than the corresponding hydrogen complex, and this will tend to cancel the effect on the activation energies of the different zero point energies in the initial state.⁵

This will reduce the relative difference in rates of the two isotopic molecules, for it is obvious that, if the zero point energy difference in both states were the same, all other factors being equal the two isotopic molecules would react at the same speed. The method used to study these reactions was that of the diffusion flame method of von Hartel and Polanyi.⁶ The initial experiments were carried out with a mixture of hydrogen and deuterium chlorides, the product of the reaction with sodium being, H and D atoms and sodium chloride. A determination of the relative amounts of hydrogen and deuterium formed, leads directly to the rates of the two reactions,



However, the possibility of the following chain reaction existed



and although this rendered the interpretation of the result difficult, a complete analysis of the reaction mechanism indicated that reactions (1) and (2) proceeded at approximately the same rate. In view of the indecisive nature of this conclusion, it was desirable to repeat the experiments, using pure DCl and HCl, and thus measure directly the rates of reactions (1) and (2).

In this way it has now been found that the activation energies of reactions (1) and (2) calculated from determinations at one temperature are 6100 and 6400 Cals. respectively. Calculation of the energy surfaces representing the reaction ⁷ have shown that the small difference in

⁴ This volume, pp. 1375 and 1400.

⁵ For further discussion see Bawn and Ogden, *Trans. Faraday Soc.*, 1934, 30, 432.

⁶ Hartel and Polanyi, *Z. physikal Chem.*, 1930, 11B, 97.

⁷ This journal, p. 1402.

activation energy is approximately equal to the difference between the zero point energies of the molecules in the transition and the initial states.

Part I.

Experimental.

The deuterium chloride was prepared by burning deuterium in excess chlorine by a method similar to that used by Dixon and Edgar.⁸ The apparatus is shown in Fig. 2. Liquid chlorine was stored in R and its entrance into the reaction vessel controlled by the nickel membrane valve V_1 . Deuterium

was allowed to flow from the storage vessel G into the reaction vessel through a fine capillary tube. The deuterium chloride formed was carefully purified from chlorine, by passing the gas backwards and forwards over boiling mercury in A. It was finally condensed in R. Hydrogen chloride was made by a similar method, and also from ammonium chloride and sulphuric acid. The concentration of deuterium chloride in mixtures of the two gases, was estimated by converting to water, the density of which, was determined by the use of a micropyknometer.⁹

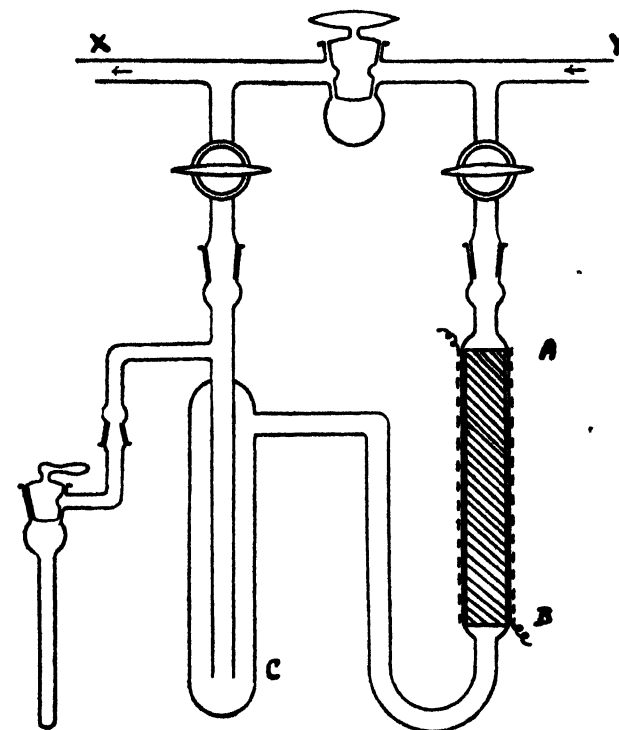


FIG. 1.—Copper oxide furnace AB for combustion of hydrogen and cooled trap C. XY main streaming line of diffusion flame apparatus.

The hydrogen chloride was first completely decomposed, by means of metallic sodium in W (Fig. 2) and the hydrogen formed was subsequently burnt to water in the copper oxide furnace C. The small quantity of sodium necessary for the above purpose was introduced into the reaction vessel W by electrolysis through the wall of the vessel.¹⁰ The amount (3-4 times excess) was estimated from the quantity of electricity passed through the cell. The water was purified by leaving in contact with

⁸ Dixon and Edgar, *Phil. Trans.*, 1906, 205A, 169.

⁹ Gilfillan and Polanyi, *Z. physikal. Chem.*, 1933, 166A, 254.

¹⁰ Márton and Rostás, *Z. techn. Physik.*, 1929, 10, 52.

sulphur for a day to remove mercury and finally by distillation from -10°C. to -30°C.

The diffusion flame apparatus and the method of carrying out the experiment have already been described.¹¹ The only modification of the apparatus was the introduction into the main streaming line of a copper oxide furnace and trap (Fig. 1). This was placed directly after the cooled traps (pumped off liquid air) used to remove the hydrogen chloride from the carrier gas. The reactions occurring in the flame liberate hydrogen and deuterium atoms which finally unite to give H_2 and HD molecules. The hydrogen thus formed passes on with the carrier gases through the copper oxide furnace, where it is completely burnt to water, which is collected in the trap (Fig. 1) immersed in liquid air. The water was then carefully purified by standing over sulphur (to remove mercury) and by distillation from -10°C. to -30°C.

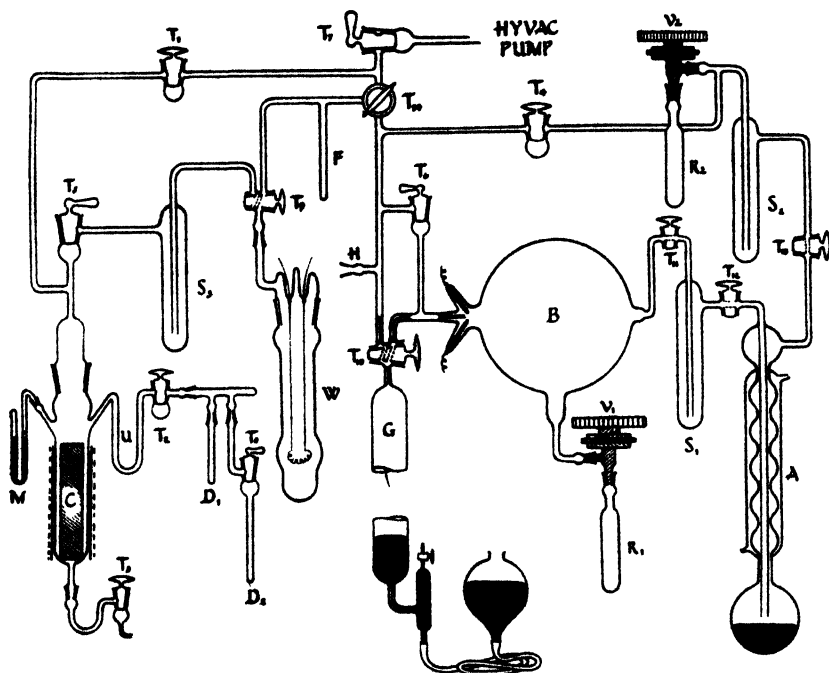


FIG. 2.

The experiments were carried out under conditions which gave rise to a measurable flame, just as in the case of reaction velocity measurements. The carrier gas was nitrogen and the temperature of the sodium and also the reaction space was maintained constant at 250°C. The flame was illuminated by means of a sodium resonance lamp and the diameter was kept at 3-4 cms. throughout the run, which usually took from 7-10 hours.

Results.

The results obtained in successive experiments are given in Table I.

A blank experiment, carried out with pure hydrogen chloride, showed that the water formed had the same density as that formed directly from

¹¹ Hartel and Polanyi, *loc. cit.*⁶; Hartel, Meer and Polanyi, *Z. physikal. Chemie*, 1932, 19B, 139.

the hydrogen chloride. Estimation of the hydrogen chloride used, and of the water formed, also showed that all the hydrogen produced by reaction with sodium was burnt in passing through the copper oxide furnace.

TABLE I.—TEMPERATURE OF REACTION ZONE 250°.

D Content of Water corresponding to Initial Hydrogen Chloride. Per Cent.	D Content of Final Water. Per Cent.
1.50	0.69
1.50	0.60

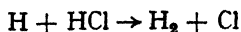
Discussion.

If it is assumed that the hydrogen is produced solely by the reactions



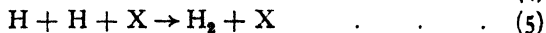
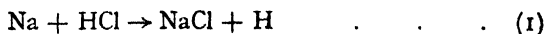
then the above result indicates that reaction (1) is 2.5 times faster than reaction (2).

However, since the hydrogen chloride is in excess in the reaction vessel, hydrogen may be formed by following reaction



together with $\text{H} + \text{H} + \text{X} \rightarrow \text{H}_2 + \text{X}$.

The reaction $\text{Cl} + \text{HCl}$ (or DCl) $\rightarrow \text{H} + \text{Cl}_2$ is energetically impossible. Hence, in the case of the mixture of hydrogen and deuterium chlorides the total reaction is



Reactions (5) and (6) will be improbable in view of the low concentration of hydrogen atoms, and may, therefore, be neglected. Confining our attention to reactions (1) and (2) and (3) and (4), it is seen that reactions (1) and (2) give rise to one hydrogen atom, which on subsequent reaction via (3) and (4) give rise to one molecule of H_2 and one molecule of HD respectively, corresponding to a ratio of one deuterium atom to three hydrogen atoms. Since the latter is the hydrogen estimated, it is obvious that the experimental method leads to a threefold concentration of the hydrogen compared to that of deuterium if the above chain mechanism is assumed. This is approximately the same as our measured concentration factor, and furthermore, since steps (3) and (4) are negligible in controlling the rate, it indicates that reactions (1) and (2) occur at the same speed.

Part II.

We have now been able to measure directly the velocities of the reactions (1) and (2). The results indicate that the velocities for hydrogen chloride and deuterium chloride are $4122 \cdot 10^{-12}$ and $3442 \cdot 10^{-12}$ c.c. $\text{mol}^{-1} \text{sec}^{-1}$ respectively, thus providing additional support for the conclusion reached above.

Experimental.

The method of carrying out the measurements was essentially the same as described by Hartel, Meer and Polanyi.¹¹ The formula used for the calculation of the velocity constant

$$k = \frac{\ln. \left(\frac{p_T}{p_0} \right)^2}{R^2} \cdot \frac{\delta}{p_{HI}}$$

where p_0 and p_T are the pressures of sodium at the nozzle and edge of the flame respectively, R is the radius of the flame, δ diffusion constant of sodium and p_{HI} the pressure of halide in reaction vessel. The formula is based on various assumptions and the accuracy of the calculated constant will depend on the extent to which these assumptions are fulfilled. An elaborate investigation of these factors, has been carried out by W. Heller and his co-workers (to be published shortly) who have determined the experimental conditions under which the above formula holds good, and in this communication it will suffice to mention them briefly. In deriving the formula it is assumed that the reaction partner pressure (HCl) is constant throughout the reaction zone, and equal to its partial pressure in the remainder of the reaction vessel. This will be determined by the linear velocity of the carrier gas leaving the nozzle, and high speeds of circulation will tend to reduce the concentration of halide directly in front of the nozzle.

On the other hand, the streaming velocity must be such that the condition of diffusion of the sodium from the nozzle holds, and also it must not be so low that back diffusion of the reaction partner into the nozzle occurs. The optimum conditions under which these assumptions are good approximations have been fixed experimentally by Heller and in the measurements reported in this paper these conditions have been closely adhered to.

Another assumption which is made is that the diffusion coefficient of sodium in the reaction gas mixture is identical with that in the pure carrier gas at the same temperature and pressure. That this also is a good approximation follows from Heller's observation that varying the partial pressure of the reaction partner from 0.1 to 3 per cent. of the total pressure caused no change in the velocity constant in several cases calculated on the basis of this assumption.

Lastly, the accuracy of the final result will be determined by the accuracy with which the measurements can be carried out. The greatest uncertainty occurs in the measurement of the flame diameter, and an accurate measurement of this is essential, since it appears in the formula for k raised to the second power. By the use of a moving cross wire mechanism with vernier attachment,* which is fixed directly to the reaction vessel, it has now been possible to reduce this error such that the inaccuracy in the measurement of the flame size is less than 1 mm. for flame of 3 cm. diameter.

Although the new experimental procedure cannot yet be assumed to give absolute values of the velocity constant, the estimated accuracy of the measured constants for both the HCl or DCl reactions is 30 per cent. However, since the two reactions were carried out under almost identical conditions the error in the relative measurement is about 15 per cent.

Results.

The results are set out in Table II.

The activation energies were calculated from the formula

$$\frac{\text{Effective no. of collisions}}{\text{Total no. of collisions}} = e^{-E/RT}$$

* A description of this instrument will be published shortly.

TABLE II.

Reaction Partner.	Pressure of Na Vapour at Nozzle, mm. 10^4 .	Temperature of Reaction Zone, $^{\circ}\text{C}$.	Streaming Velocity of Nitrogen, mol./sec. 10^4 .	Rate of Flow of Reaction Partner, mol./sec. 10^4 .	Total Pressure in Vessel, mm.	Partial Pressure of Reaction Partner, mm.	Diffusion Coefficient of Sodium, mol./cm. ² /sec.	Radius of Flame, cm.	Velocity Constant, cc. mol. ⁻¹ sec. ⁻¹ $\cdot 10^{11}$.	Activation Energy, Cal.	Mean Activation Energy, Cal.
HCl	3.105	238	1.393	67.79	3.493	.1621	136.7	1.29	.5319	5953	6100
	3.105	238	1.405	124.4	3.513	.2859	135.8	1.07	.4354	6156	
	3.105	238	1.398	109.1	3.532	.2557	135.1	1.27	.3438	6400	
	3.698	238	1.507	97.88	3.689	.225	129.4	1.26	.4036	6236	
	3.954	238	1.518	67.63	3.709	.1581	128.7	1.2	.6442	5757	
	3.950	238	1.201	63.84	3.870	.195	123.3	1.31	.4192	6197	
	3.954	238	1.298	45.02	3.493	.117	136.7	1.52	.5765	5870	
	3.954	238	1.447	180.1	3.571	.3954	133.7	1.06	.3431	6402	
DCI	3.105	238	1.396	162.6	3.454	.3602	138.1	1.12	.3208	6472	6400
	2.979	238	1.329	77.78	3.428	.1895	139.2	1.41	.3820	6292	
	2.979	238	1.324	124.4	3.428	.2944	139.2	1.15	.3698	6325	
	2.094	236	1.385	142.1	3.473	.3232	136.6	1.14	.2948	6527	
	2.979	238	1.383	124.4	3.454	.2851	138.1	1.10	.4140	6209	
	4.819	238	1.575	155	3.850	.3449	123.9	1.24	.2841	6593	

The total number of collisions was calculated in the usual way, using a collision diameter 3.4×10^{-8} cm. for both reactions. The experimental accuracy of the activation energy is ± 300 Cals., and although this is about the same as the difference in value for HCl and DCl, we are justified by taking the mean of several series of results to assume that the hydrogen chloride reacts slightly faster than the deuterium chloride.

Discussion.

The important conclusion reached from the foregoing results, is that the reaction rates of hydrogen and deuterium chloride with sodium are very nearly the same. The activation energies as calculated from the reaction rates differ by only 300 Cals. whereas, if the full zero point energies were operative the expected difference in the activation energies would be 1200 cals. The result is readily understandable, by a consideration of the potential energy surfaces given in the paper of Evans and Evans, and published in this number of the journal (p. 1400). It is shown that the activation energy of the reaction is made up of the energy required to bring up the sodium atom to within some critical distance of the chlorine of the hydrogen chloride and the energy to expand the H—Cl bond to such a point that the potential energy of the system $\text{Na} \dots \text{Cl} \dots \text{H}$ is the same as that of $\text{Na}^+ \dots \text{Cl}^- \dots \text{H}$. The first part of the process has little influence on the H—Cl bond, and thus the zero point energy difference will not enter into this energy, and this difference will not affect the critical distance to which the sodium must be brought. It is shown that the second part of the process—the passage of the chlorine atom from the hydrogen or deuterium atom to the sodium atom to form Na^+Cl^- involves a very small activation energy. It is in this latter step that any difference in zero point energy will manifest itself. The fraction of the total energy of the bond which was taken as coulombic is important here. Although an increase of the coulombic decreases slightly the total activation energy, it increases the fraction of the total activation energy which involves the splitting of the H—Cl bond. By taking 20 per cent. as the coulombic fraction, a reasonable activation energy was obtained most of which was due to the bringing up of the sodium to the hydrogen chloride. It is assumed, therefore, that when the sodium reaches the critical distance the chlorine passes from the hydrogen to it without any further expenditure of energy. The difference in rates of reaction will now be given by the difference in energy of the zero levels in the initial and critical states of the HCl and DCl molecules. This will be the difference in zero point energy introduced by change of shape of the potential energy curve, in passing from the initial to the transition state.

If ΔE_0 is the zero point energy difference in the initial state and ΔE_1 the zero point energy difference in the transition state when hydrogen chloride is at the critical distance from the sodium atom, the difference in activation energy for the two isotopic reactions will be $\Delta E_0 - \Delta E_1$. The estimation of ΔE_1 was made by fitting a parabola to the potential curve corresponding to the critical state. From the equation of this parabola $r^2 = 4kV$ where V is the potential energy, k can be obtained, and since

$$\nu = \frac{1}{2\pi} \sqrt{\frac{4k}{\mu}},$$

the zero point energy E_0 is equal to

$$E_0 = \frac{1}{4\pi} h \cdot \sqrt{\frac{4k}{\mu}},$$

where μ is the reduced mass. The value for ΔE_1 so obtained is 750 Cals.

A similar estimation of ΔE_1 obtained by fitting a parabola to the lower portion of the Morse HCl curves give $\Delta E_0 = 1200$, which agrees extremely well with the value obtained from spectroscopic data, namely 1184 Cals. Hence $\Delta E_0 - \Delta E_1 = 1200 - 750 = 450$ Cals, compared with the experimental value of 300 Cals.

Summary.

The velocities of reaction of atomic sodium with hydrogen and deuterium chlorides, *viz.* :



have been measured. It has been found that the activation energies of these reactions differ by 300 Cals. This has been shown to be approximately equal to the difference in zero point energies of the reacting molecules in the initial and in the transition state.

Our best thanks are due to Professor M. Polanyi for his advice and interest in this work ; and to the Department of Scientific and Industrial Research for a grant to one of us (A. G. E.).

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THE MECHANISM OF REACTIONS BETWEEN ALKALI ATOMS AND HALOGEN HYDRIDES.

BY A. G. EVANS and M. G. EVANS.

Received 4th July, 1935.

Schay¹ and von Hartel² have determined the velocity, activation energies and collision diameters for the reactions of atomic sodium and potassium with the halogen hydrides. Bawn and Evans³ have determined the activation energies for the reaction between sodium and hydrogen chloride and deuterium chloride. It is the work of these latter authors which has occasioned this theoretical discussion. The experimental results can be summarised as follows :

1. Von Hartel and Schay found that the reaction velocities of the halogen hydrides followed the same order as the heats of reaction of the different members of the series.

2. In those cases where the heats of reaction were positive it was found that to account for the observed velocities, enhanced collision diameters had to be introduced into the gas kinetic expression.

¹ *Z. physik. Chem.*, 1930, (B11), 291.

² *Ibid.*, 1930, (B11), 316.

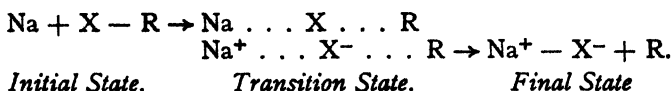
³ Bawn and Evans. This vol. p. 1392.

3. The experiments of Bawn and Evans have shown that the rates of reaction between sodium atoms and hydrogen chloride and deuterium chloride are approximately the same, the activation energy for the two being 6100 cal. for hydrogen chloride and 6500 cal. for deuterium chloride. It is of great interest that the full zero point energy difference between HCl and DCl which is ~ 1500 cal., does not appear in the difference in activation energy.

In two recent publications, Ogg and Polanyi⁴ have put forward a theory of ionogenic reactions and a method to calculate their activation energies. In this communication we wish to apply this method to the reactions between alkali atoms and halogen hydrides.

The Activation Energy of Ionogenic Reactions.

Ogg and Polanyi have shown that the reactions of the type we are discussing can be represented by the superposition of two energy surfaces: one relating to the reaction process in which homopolar forces are operative and the other to an ionic state; the reaction occurring in a state represented by a point on the intersection line of these two surfaces. We can represent these two phases in the reaction process:—



The two surfaces $(\text{Na} \dots \text{X} \dots \text{R})_h$ the homopolar surface, and $(\text{Na} \dots \text{X} \dots \text{R})_i$ the ionic surface correspond to these two phases of the reaction process. The transition state will be a mixed state, and will be represented by an eigenfunction ψ which will be a linear combination of the eigenfunction of the two pure states ψ_1 and ψ_2 . $\psi = a_1\psi_1 + a_2\psi_2$ where if ψ_1 and ψ_2 are dependent on the space co-ordinates only, the coefficients a_1 and a_2 will include the time dependence and will obey the normalising condition $a_1a_1 + a_2a_2 = 1$. At the point of intersection of the two surfaces, which can be characterised by some function of the co-ordinates $f(r)$, the two states ψ_1 and ψ_2 are completely degenerate, the eigenvalues ϵ_1 and ϵ_2 of the energy operator, being equal at this point. The linear combination of the pure states in which we are chiefly interested will be the one leading to the lowest energy surface, *viz.*,

$\psi = \frac{1}{\sqrt{2}}(\psi_1 + \psi_2)$ and the eigenvalue of the energy operator will lead to

the true value of the energy in the mixed state. This will be lower than the value at the crossing point by an amount given by the matrix $\int \psi_1 H \psi_2 d\tau = \epsilon_{12}$, where H is the energy operator. We shall discuss in a later section the probability of transition from the state ψ_1 to state ψ_2 , a factor which is important when considering the temperature independent factors of these reactions and the probability of the transition state. For this we shall require the total splitting of the two states ψ_1 and ψ_2 which is the difference in eigenvalue between the lower linear combination

$\psi = \frac{1}{\sqrt{2}}(\psi_1 + \psi_2)$ and the repulsive state $\psi = \frac{1}{\sqrt{2}}(\psi_1 - \psi_2)$. The

total "splitting" is clearly twice the matrix element, *viz.*, $2\epsilon_{12}$, and is called the perturbation energy W in the papers of Ogg and Polanyi.

⁴ Ogg and Polanyi, *Proc. Manchester Lit. and Phil.*, 1934, 78, 41; *Trans. Far. Soc.*, 1935, 31, 604; and this vol., p. 1375.

The Calculation of the Activation Energy.

The energy surface was first constructed for the homopolar reaction between the atoms $(\text{Alk}-\text{Hal}-\text{H})_n$. The whole of this surface is not required for our present purpose, but it is found, as one would expect from *a priori* consideration, that if the reaction were to proceed homopolarly to form a homopolar alkali halide molecule (which would determine the activation energy) with a subsequent and non-rate determining change of the alkali halide to the polar form, then the activation energy required for this mechanism would be far in excess of that actually observed, *e.g.*, $\text{Na} + \text{Cl}-\text{H} \rightarrow \text{Na}-\text{Cl} + \text{H} \rightarrow \text{Na}^+-\text{Cl}^- + \text{H}$, and we feel

justified, therefore, in excluding this mechanism. This is seen in Fig. 1, which shows the final state of the homopolar surface in faint contours lying very much higher in energy than the final polar state, and necessitating for its formation a large activation energy.

The second energy surface which we require is the polar surface $(\text{Alk}^+ \dots \text{Hal}^- \dots \text{H})_n$, and we can construct this by considering the approach of a hydrogen atom to the polar alkali halide molecule for various separations of the alkali halide

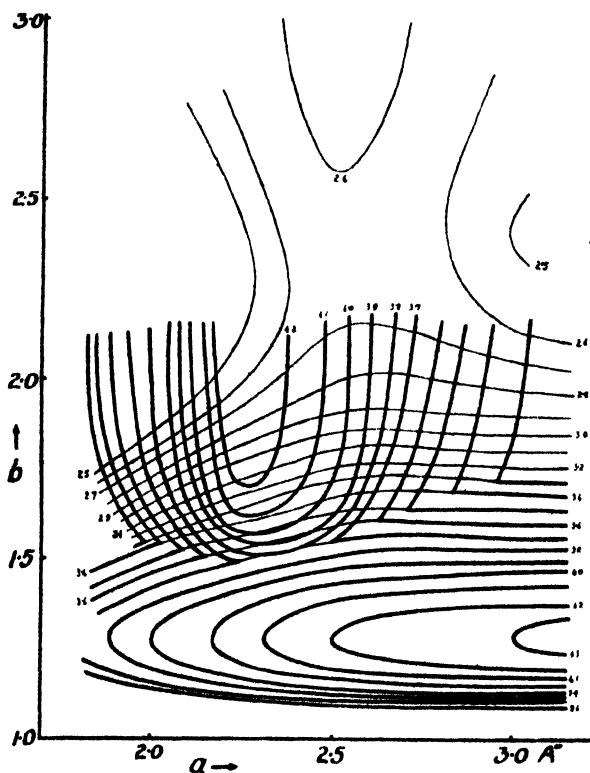


FIG. 1.

nuclei. In this way we actually construct a number of sections through the energy surface at constant $(\text{Alk}-\text{Hal})$ separation. The forces with which we are concerned in constructing such sections are a small attraction arising from the polarisability of the hydrogen atom and the charges on the halide and alkali atoms, and repulsion forces (which will be overwhelmingly large at small separation) due to forcing together the hydrogen atom and the negative halide ion which will behave like an inert gas atom. The energy of the alkali halide molecule at the various ionic separations will remain constant for any given section and will fix the position of the various sections relative to each other. The two surfaces obtained in this way are superimposed in such a way that the

heat of reaction is the difference in levels between the initial and final states. The heat of reaction Q is made up from the following terms:—

$$Q = (D_2 - \frac{1}{2}h\nu_2) - (D_1 - \frac{1}{2}h\nu_1) + \epsilon_{\text{Hal}} - I_{\text{alk.}}$$

where the separate terms are defined by the following thermal equations,

$\text{H} - \text{Hal} = \text{H} + \text{Hal}$	$-(D_1 - \frac{1}{2}h\nu_1)$	D_1 depth of potential curve. $\frac{1}{2}h\nu_1$ zero point energy of $\text{H} - \text{Hal}$.
$\text{Hal} + \epsilon = \text{Hal}^-$	$+\epsilon_{\text{Hal}}$	ϵ_{Hal} electron affinity of the halogen.
$\text{Alk} = \text{Alk}^+ - \epsilon$	$-I_{\text{alk}}$	I_{alk} ionisation potential of the alkali metal.
$\text{Alk}^+ + \text{Hal}^- = \text{Alk} + \text{Hal}$	$+(D_2 - \frac{1}{2}h\nu_2)$	D_2 depth of potential curve. $\frac{1}{2}h\nu_2$ zero point energy of $\text{Alk} + \text{Hal}^-$.

TABLE I.

Compound.	$r_e \text{ \AA.}$	$\omega_e \text{ cm.}^{-1}$	$\nu_e \omega_e \text{ cm.}^{-1}$	$D \text{ volt.}$	$a \text{ cm.}^{-1}$	Compound.	$r_e \text{ \AA.}$	$b \times 10^{18}$.
HCl	1.272*	2989.68*	51.90*	4.56	1.750	Na+Cl-	2.35	1.045
HBr	1.411*	2647*	44*	3.84	1.768	Na+Br-	2.47	2.241
HI	1.617*			3.13†	2.28†	Na+I-	2.66	3.987
NaH	1.90*	874.6*	10.48*	2.25*	.78	K+Cl-	2.66	3.987
KH	2.26*			2.14	.78	K+Br-	2.78	5.753
						K+I-	2.97	9.636

* Jevons, "Report on Band Spectra."

† Ekstein and Polanyi, *Z. physik. Chem.*, 1932, **B15**, 337.

The r_e for these compounds were computed by the Clarke rule for homopolar bonds $r_{AB} = \frac{1}{2}(r_{AA} + r_{BB})$.

Numerical Calculation.

We have applied the method described above to the calculation of the energy surfaces and activation energies for the reactions between sodium and potassium atoms and the halogen hydrides.

The potential energy curves for the homopolar molecules were calculated from the semi-empirical relations given by Morse and Table I. gives the constants we have used for the various molecules. The potential energy curves for the polar molecules were obtained in the manner described by Pauling,⁵ the equation of the curves being made up of two factors: one an attraction term due to the electrical attraction of the two charges, and secondly a repulsion term due to the compression of the two inert gas atom shells. The constant b of the repulsion term br^{-9} was chosen so that the resultant curve gave the internuclear spacing of the alkali halide molecule at the minimum of potential energy. The spacings used were obtained from Huggin's and Mayer's⁶ value for $(r_+ + r_-)$ for alkali halides.

The forces between the hydrogen atom and polar alkali halide were calculated in the usual way, using an equation of the form

$$E = -\frac{\alpha e^2}{2r^4} + br^{-9},$$

⁵ Pauling, *J. Amer. Chem. Soc.*, 1932, **54**, 998.

⁶ Huggin and Mayer, *J. Chem. Physics*, 1933, **1**, 643.

where α is the polarisability of the hydrogen atom. The choice of the constant b is of some importance, and the value we chose was that which gave the correct internuclear spacing for the $H^+ Hal^-$ potential curves.* We feel that this value of b would not differ widely from the value necessary for the correct form of the potential curve, and would be more reasonable than some arbitrarily chosen b ; such a choice will certainly lead to consistency in the comparisons between the various halogen halide reactions.

The homopolar energy surface already described was calculated by means of the energy equation for three atoms.⁷

$$E = A + B + C + \sqrt{\frac{1}{2}\{(\alpha - \beta)^2 + (\alpha - \gamma)^2 + (\beta - \gamma)^2\}},$$

where the Roman letters represent the coulombic part of the total energy of binding and the Greek letters the interchange energy. The fraction of the total energy taken as coulombic was varied according to

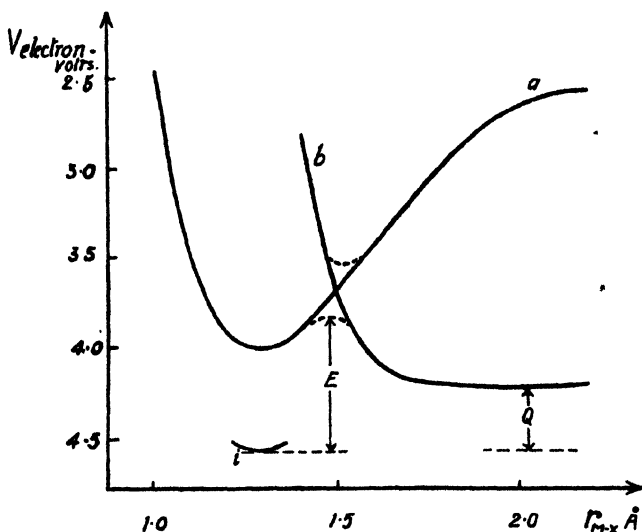


FIG. 2.

the atomic number of the atoms concerned in the molecules. Rosen⁸ has pointed out that there exists such a connection, the fraction of coulombic energy increasing with increasing atomic number, and that whereas for H_2 the coulombic fraction may be 10-14 per cent. of the total energy, for alkali molecules

Na_2 the coulombic fraction may be as large as 20-30 per cent. of the total. We have taken various percentages for the value of the coulombic fraction in those cases where large uncertainty exists, in order to determine if the effect of varying coulombic fractions is very marked upon the activation energy. We will discuss this point again later.

In Fig. 2 we give the diagram for one particular case, sodium and hydrogen chloride, in order to illustrate the method. Curve a shows the section through the energy surface for the homopolar reaction at a constant sodium-chlorine distance of 2.25 Å. This distance does not give the lowest activation energy for the homopolar reaction, this being given at a distance of 2.75 Å and leads to an activation energy of 1.7 volts.

* The forces between the Na^+ and the hydrogen are negligible when considering the configuration $Na^+ Hal^- H$.

⁷ Eyring and Polanyi, *Z. physik. Chem.*, 1931, B(12), 279.

⁸ Rosen and Ikehara, *Physic. Rev.*, 1933, 43, 5.

TABLE II.

Reaction.	r_{M-X} (At Crossing Point.)		Activation Energy Observed. Cals.	Heat of Reaction. Cals.	Activation Energy Calcul. Cals.	Increased Probability of Collided State. $e^{-E/RT}$ E (in cal.).
	Å.	Å.				
Na, HCl	2.35	1.50	- 6-7000	- 5000	- 12,000	—
Na, HBr	2.70	1.65	- 1500	- 1600	- 4500	—
Na, HI	2.70	1.75	+ 1100	0	—	900
K, HCl	2.75	1.48	- 800	- 2200	- 9000	—
K, HBr	2.95	1.63	+ 800	+ 1600	—	460
K, HI	3.30	1.81	+ 3000	+ 5000	—	2500

On this curve we have superimposed curve *b*, which is the potential energy curve for the repulsion between a hydrogen atom and a polar $\text{Na}^+ \text{Cl}^-$ molecule. The portion of curve (*i*) shown on the diagram represents the minimum energy of the initial state when the sodium is at infinite distance from the hydrogen chloride, and the repulsion curve is placed in the diagram in such a position that the heat of reaction is given by *Q* in the manner we have already described.

The activation energy of the process was determined by taking a large number of sections similar to Fig. 2 and choosing that section for which the height *E* from the lowest vibrational level on curve *i* to the crossing of the levels is a minimum. As we have pointed out, the transition state will not be a pure state, but a mixed state, and this will lead to a decrease of the energy of the transition state below that represented by the actual crossing point. The dotted line in Fig. 2 represents this decrease in the energy of the transition state due to degeneracy of the system.

By this method we have calculated the activation energies for the reaction between alkali metals and halogen hydrides, and the results are tabulated in Table II. The uncertainty introduced into the absolute values of the activation energy will be due to two main causes.

(a) The difficulty of estimating the exact lowering of the energy of the transition state due to degeneracy (estimated $\frac{1}{2}W \sim 3000$ cal.); and

(b) The sensitivity of the rising portion of the curve (*b*) to the value of the constant in the repulsion term br^{-9} . Although the absolute values may be uncertain, we feel, however, that the comparisons between the members of the series are much more exact.

It was found that changing the fraction of coulombic energy of the homopolar alkali halide molecule did not have a pronounced effect on the *total* activation energy of the reactions.

Collision Diameters.

Schay found that when using a collision diameter of ~ 3.6 Å (for reactions between alkali metal atoms and halogen hydrides) the experimental velocity constants for the reactions between sodium and hydrogen iodide and potassium and hydrogen bromide and hydrogen iodide were larger than those calculated on the kinetic theory basis. It is doubtful,

however, whether a value of 3.6 Å for the collision diameter represents the real nature of a collision between molecules of this kind, and we have made some attempt to calculate the forces which operate in collisions of this type.

The collision diameter of a molecule can be related to a normal diameter of a hard sphere and to the Sutherland constant, which is a function of the attractive and repulsive potentials between the colliding molecules, by the relation :—

$$Q_{\text{calc.}} = Q \left(1 + \frac{S}{273} \right),$$

where Q is the diameter of the molecule when no forces operate and S the Sutherland constant. The forces between the colliding molecules will be of two kinds : (1) a repulsive force, which is normally considered, and increases extremely rapidly at small distances ; (2) and an attractive force which is responsible for van der Waals' adsorption effects and deviations from the perfect gas law, and it is these attractive forces in which we are interested in this discussion. There are two main methods of calculating these forces theoretically, one by London⁹ and Eisenschitz,¹⁰ and the other by Eyring. London and Eisenschitz obtain an expression for the attractive field between two atoms or molecules when there is no valency binding, which they show can be related to the ionisation potentials of the atoms or molecules, and to their polarisabilities :—

$$\epsilon = \frac{3}{2} \frac{I_1 I_2}{I_1 + I_2} \alpha_1 \alpha_2,$$

where I_1 and I_2 are the ionisation potentials and α_1 and α_2 the polarisabilities of the molecules. In this way they are able to calculate the potential field between two mercury atoms and mercury and argon atoms to a high degree of accuracy.

The method used by Eyring¹¹ is to consider the collision of two molecules when the bond between the atoms forming the individual molecules is not affected. Such a restriction, together with the assumption that the other forces are small compared with these binding forces, reduces the equation for the potential energy between four atoms to the form :—

$$E = A_1 + A_2 + B_1 + B_2 + C_1 + C_2 + \alpha_1 + \alpha_2 - \frac{1}{2}(\beta_1 + \beta_2 + \gamma_1 + \gamma_2)$$

where the Roman letters are coulombic integrals and the Greek letters the interchange integrals. Since $A_1 + \alpha_1$ and $A_2 + \alpha_2$, the integrals for the two molecular bonds remain constant throughout the collision process the energy of collision reduces to :—

$$E = B_1 + B_2 + C_1 + C_2 - \frac{1}{2}(\beta_1 + \beta_2 + \gamma_1 + \gamma_2).$$

From this expression it is seen that the forces which are tending to increase the cohesion between the molecules are the coulombic forces, and these are just the forces which London and Eisenschitz have employed in their expression for the van der Waals' attraction. The greater the polarisability of the molecules the greater will be the attractive potential and the greater will be the contribution to the coulombic

⁹ London, *Z. physik. Chem.*, 1930, B11, 222.

¹⁰ London and Eisenschitz, *Z. Physik*, 1930, 60, 520.

¹¹ Eyring, *J.A.C.S.*, 1932, 54, 3191.

integral, and hence the greater will be the attractive potential on the basis of Eyring's expression.

We have calculated on the basis of both these expressions the collision potential for the reactions under consideration. This collision potential will become evident on the potential energy surface, and will, in those cases where it is sufficiently well marked, lead to a small potential hollow in the collided configuration. In most ordinary chemical reactions such considerations as these do not enter in, since the activation energy of reaction is sufficiently large to allow us to neglect the increased probability of the collided state.

We find that this increased probability of the collided state becomes significant in the reactions between sodium and hydrogen iodide and potassium and hydrogen bromide and iodide. It is not surprising that this should occur as the heat of reaction becomes increasingly exothermic, since the heat of reaction, polarisability and the coulombic fraction of total binding energy are all interconnected. There are three factors which are mainly responsible for the change in heat of reaction as one proceeds along the series keeping the alkali metal the same. The large decrease in the bond strengths of the halogen hydride is offset by the smaller decrease in electron affinity of the halogen atom and decrease in the bond strength of the polar $M^+ X^-$ molecule. It is therefore the decrease in bond strength of the halogen hydride which is mainly responsible for the decrease in the endothermicity of the reaction.

	Bond Energy Volts.	Ionisation Potential Volts.	Polarisability.
H Cl	4.38	13.8	2.63×10^{-24}
H Br	3.56	13.2	3.58×10^{-24}
HI	2.99	12.8	5.39×10^{-24}

The ionisation potential of these molecules follows the same order as the bond strength, and as one should expect the polarisability increases as the ionisation potential decreases. It is also clear that the coulombic integral will increase in its ratio to the interchange integral as the ionisation potential decreases. The table gives the ratios of coulombic to total energy for S electrons and different quantum number taken from the work of Rosen, to which we have already referred.

Quantum number n	.	1	2	3	4	5
Per cent. coulombic	.	12	23	29	39	45

Although in the present discussion we have not been concerned solely with S electrons, the same type of regularity will appear.

There are, therefore, the following factors which tend to increase the reaction velocity as the exothermicity of the reaction increases.

- (a) There is the connection between the heat of reaction and the activation energy, a theorem which has been deduced by Ogg and Polanyi.

The cases which we have examined are in reality a combination of the two cases given in their paper. In changing from sodium to potassium or from one halogen hydride to another, the energy change for the reaction is composite, being made up of changes in the halogen hydride bond strength—the ionisation potential of the alkali metal and the

electron affinity of the halogen, and the alkali halide bond strength. The sum of these changes, *i.e.*, the heat of reaction, can be used to move either the *a* or *b* curve along the potential energy axis. Other changes, such as slight alterations in the shape of the curve *a* or *b*, will be minor compared with this main change.

- (*b*) Connected with this change in heat of reaction there is, as we have shown, a change in the polarisability and the coulombic integral which affects the probability of the collided state.

Using the increased probability of the collided state as obtained from these calculations, we have recalculated the theoretical velocity constants, and the Table II. gives the results of the comparison of the theoretical and observed activation energies. The increased collision diameter calculated by Schay on the basis of a normal collision diameter of 3.6 Å is very closely accounted for by the increased probability of the collided state that results from the considerations described above.

In discussing reactions of alkyl halides with sodium atoms, Hartel and Polanyi¹² reached similar conclusions, starting from a slightly different point of view. They suggest that the larger coulombic binding, together with the smaller bond strengths, may account for the trend in activation energy as the central atom in the configuration Alk — Hal — Na changes from fluorine to iodine.

Relative Rates of Reaction of Hydrogen and Deuterium Halides with Sodium.

In the cases we have considered, it is clear that where the activation energy is extremely small, or where the reaction occurs with a greatly enhanced collision diameter, we should expect little or no difference in the velocities of the hydrogen and deuterium halide. This has been experimentally realised by the work of Bawn and Evans. It appears from our previous discussion that the activation energy is separable into two distinct parts (*a*) that which is required to bring the sodium atom up to the hydrogen halide molecule, and (*b*) that required for the expansion of the H — Hal bond to the configuration of the transition state. It is the first process which chiefly contributes to the total activation energy in those cases which show a real positive activation energy. This process will also require a smaller amount of energy the larger the halogen atom becomes and the greater the coulombic fraction of the total binding energy. The subsequent extension of the Hydrogen-Halogen bond requires very little further expenditure of energy, and in the cases examined theoretically this second process requires a negligible amount of energy over and above that for the first process.

It has been pointed out by Polanyi¹³ that the difference in activation energies of reactions of isotopic molecules, will be determined by the difference in zero point energies in the transition state as well as their difference in the initial state. In these reactions the transition state is reached without any appreciable extension of the hydrogen halide bond, and so the difference in zero point energies of the two isotopic systems in the transition state will be practically the same as their difference in zero point energy in the initial state. Hence, we should expect the activation energies to be practically identical.

¹² Hartel and Polanyi, *Z. physik. Chem.*, 1931, B11, 97.

¹³ *Nature*, 1934, 133, 26.

Any differences in velocity which are made manifest in comparing hydrogen and deuterium compounds will arise from the changes in zero point energy difference which occur in the first step of the reaction process. These changes will be brought about by changes in the zero point levels for the difference molecules due to the change in shape of the cross section for H — Hal vibration as the system passes from state i to state a . As the system passes from i to a the force constant for the vibration H — Hal becomes smaller, thus changing the zero point difference

$$\frac{1}{2}(h\nu_1 - h\nu_2) = \frac{h\sqrt{k_1}}{2\pi} \left(\frac{1}{\sqrt{M_1}} - \frac{1}{\sqrt{M_2}} \right)$$

for the initial state to

$$\frac{1}{2}(h\nu_1^1 - h\nu_2^1) = \frac{h\sqrt{k_2}}{2\pi} \left(\frac{1}{\sqrt{M_1}} - \frac{1}{\sqrt{M_2}} \right)$$

for the state (a). We should expect a smaller difference in velocity as we proceed up the series towards hydrogen iodide and potassium, since, as we have pointed out, in the case of HCl and Na the H — Cl curve is much more profoundly modified by bringing up the alkali atom than for the higher members of the series.

Crossing of Levels and the Probability of Reaction.

It is generally considered that in reactions which occur by non-adiabatic change from one ψ function to another there will be an added impedance to the reaction velocity due to the probability factor connected with the change of state at the crossing of the levels which is the transition state.

London,¹⁴ for example, finds that there is a very small probability for the reaction



This small probability is connected with the degree of splitting of the crossed levels. If the separation is large, then the reaction can be considered as proceeding entirely along the lower energy surface. This becomes apparent from the

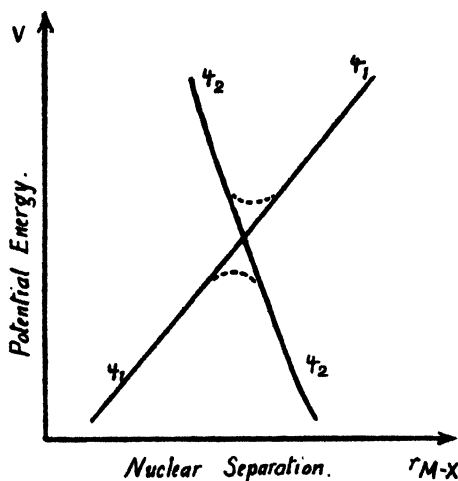


FIG. 3.

expression developed by both Landau¹⁵ and Zener¹⁶ for the probability of non-adiabatic transition. If (see Fig. 3) ψ_1 and ψ_2 are the eigen functions of the two states, for example, a homopolar state and a repulsive polar state, and ϵ_1 and ϵ_2 are the eigen values of these two states,

¹⁴ London, *Z. Physik.*, 1932, **74**, 143.

¹⁵ Landau, *Physik. Zeit. Sowjetunion*, 1932, **1**, 88; *ibid.*, 1932, **2**, 46.

¹⁶ Zener, *Proc. Roy. Soc.*, 1932, **A137**, 696; *ibid.*, 1933, **A140**, 660.

then the probability of transition from the one state to the other as r passes once through the crossing point r_0 can be expressed by

$$P_{12} = \frac{4\pi\epsilon_{12}^2}{\hbar v(S_1 - S_2)},$$

where $2\epsilon_{12}$ is the splitting of the levels at the crossing point due to the degeneracy of the system, and will be given by the matrix $\int \bar{\psi}_1 H \psi_2 d\tau$ where H is the perturbation operator. S_1 and S_2 are related to the slopes of the potential energy levels at $r = r_0$, $S_1 = \frac{dV_1(r_0)}{dr}$, and v the

velocity of the particle $v = \sqrt{2(E - V_0)/m}$. There are two points of interest in this expression, the one which we have already referred to that the probability increases as the splitting of the levels becomes more pronounced, and secondly, that for a given system and for a given vibrational energy level $(E - V_0)$ the probability of transition will be proportional to the square root of the mass of the particle, or rather the reduced mass of the moving particle. We should expect, therefore, in cases where the reaction possesses an added inertia due to this probability factor, that such a transition would be 1.4 times more probable in the case of a deuterium atom as the moving mass than in the case of a hydrogen atom. Such a difference would tend to offset differences in the zero point levels of the two compounds in the initial state.

Summary.

The mechanism of the reactions between alkali metal vapours and halogen hydrides is discussed in detail and the calculated results are compared with those obtained experimentally.

The probability of the collided state has been substituted for the ordinary classical collision number and the enhanced collision number is accounted for by a consideration of the van der Waals attraction forces. These forces are related to the polarisability of the molecules and the coulombic integrals.

The influence of the heat of reaction on the activation energy and the collision probability becomes apparent from this method of treatment. The relative rates of reaction of hydrogen and deuterium compounds are discussed with reference to these reactions and also with reference to the probability of transition at the crossing of "non adiabatic" levels.

The authors wish to thank Professor M. Polanyi for his great interest in this work, and also the Department of Scientific and Industrial Research for a grant to one of us (A. G. E.).

ON THE PHOTO-DISSOCIATION OF SINGLE CRYSTALS OF SOME NITRATES IN POLARISED LIGHT.

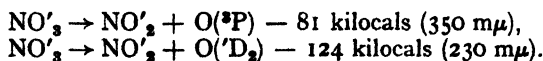
By L. K. NARAYANSWAMY, M.Sc.

(Nagpur University Research Scholar, Indian Association for the Cultivation of Science.)

Received 8th July, 1935.

I. Introduction.

In a recent paper¹ Krishnan and Guha have attributed the two ultra-violet absorption bands of inorganic nitrates in aqueous solution to the following photo-dissociations :



The appearance of these two bands in practically the same positions in the absorption spectra of solid nitrates as well, suggests that in the solids also, the absorptions should be attributed to the same photo-dissociations.

Experimenting with single crystals of sodium and potassium nitrates, in which the NO_3' ions are oriented parallel to one another, Krishnan and Dasgupta² observed that both the absorption bands are strongly polarised, light-vibrations normal to the NO_3' planes being much less absorbed than vibrations in the plane. This result has been interpreted by Krishnan and Guha as indicating a smaller efficiency of dissociation for the former light vibrations than for the latter. The present paper gives an account of an experimental study of the photo-dissociation of solid nitrates, and particularly of single crystals, with a view to verify the above conclusions.

II. Photo-Dissociation in the Solid State.

Various inorganic nitrates were finely powdered and suitably exposed to the light of a quartz mercury arc. They were then removed, and after some time tested for the presence of the nitrite, with an acetified solution of KI and starch. All of them showed a dissociation into the nitrite, though to unequal extents. The degree of dissociation diminishes in the order, K, Na, Sr, Ba, Cd, Al, Pb, and NH_4 nitrates, KNO_3 dissociating much more readily than the other nitrates. The radiations from the mercury arc extended up to about 220 m μ . The interposition of a filter which cut out all the radiations of wave-lengths shorter than 250 m μ prevented the dissociation of the nitrates almost completely, showing that the long wave-length limit of the photo-active region should be lower than 250 m μ . (For want of a monochromator, the actual limit was not determined.)

III. Depth to which Dissociation Extends in the Crystals.

Experiments with large single crystals of potassium nitrate, exposed to the arc, show that the presence of the nitrite is confined to a thin surface

¹ *Current Science*, 1934, 2, 476; *Proc. Ind. Acad. Sc.*, 1934, 1, 242.

² *Nature*, 1930, 126, 12; *Ind. J. Physics*, 1933, 8, 49.

layer on the exposed side. This short depth to which permanent dissociation extends may be due to the rapid attenuation of the exciting light by strong absorption by the crystal. (The amount of *nitrite* present, even after our longest exposure, was quite insufficient to exert a strong absorption.) It is also possible that in the interior of the crystal, owing to the accumulation of the dissociation products, they recombine, and the limit to the depth at which the nitrite could be detected is determined by the facility for escape of oxygen. The following experiments apparently favour the latter explanation.

(i) Two similar large sized plates of KNO_3 were exposed under similar conditions to the light of the mercury arc through a suitable small aperture placed immediately in front of the crystals. Whereas on one plate the whole exposure, extending to 12 hours, was given in the same place, on the other plate the exposure was given at three different places by suitably shifting the plate laterally after every 4 hours. It was found that the latter crystal had dissociated considerably more than the former.

(ii) Two large plates of KNO_3 parallel to (010) were mounted behind two similar apertures, which served to limit equally the cross-section of the irradiating beams. Whereas one of the plates was mounted so as to receive the light normally, the other plate was mounted so as to make the angle of incidence 45° , the 'c' axis being kept perpendicular to the plane of incidence.* It was found that the inclined plate was dissociated more than the other (in spite of the fact that for inclined incidence the loss due to reflection must be slightly more).

These two experiments suggest that the nearness of the irradiated molecules to the surface of the crystal is favourable for dissociation.

IV. Photo-Dissociation of Single Crystals in Polarised Light.

For studying the dependence of the photo-dissociation on the direction of vibration of the exciting light with reference to the NO_2 planes, nitrates of potassium and ammonium are very suitable. Both the crystals are ortho-rhombic, and are usually in the form of long prisms parallel to the 'c' axis. It is known from X-ray studies that the planes of the NO_2 ions in these crystals are all parallel to one another and perpendicular to the 'c' axis.

The light from a horizontal mercury arc, after passing through a quartz lens and a quartz double-image prism (of the Wollaston type) formed two images of the arc side by side, and of equal intensity, one polarised parallel to the length of the image and the other perpendicular to it. A long prism of KNO_3 of uniform thickness was cut into equal portions, and one of them was placed in the centre of one of the images and the other in the centre of the other image. The lengths of the two crystals were parallel to each other and also parallel to the lengths of the images (in some experiments perpendicular to the lengths of the images).

It was found that the crystal that was illuminated by light vibrating along the 'c' axis was dissociated much less than the other crystal. This shows that light vibrating along the normal to the plane of the NO_2 ions is much less efficient in dissociating the ions than light vibrating along directions in the plane of the ions.

Similar results were obtained with single crystals of ammonium and sodium nitrates also.

The author wishes to express his grateful thanks to Professor K. S. Krishnan for his keen interest and guidance, and to the Nagpur University for the award of a research scholarship.

* The reason for this differentiation between the 'c' and the 'a' axes will be clear from the next section. Whereas both the principal vibrations in the crystal normal to the 'c' axis are equally effective photo-chemically, those normal to 'a' are not.

THE SURFACE TENSIONS OF TERNARY SOLUTIONS. PART I. THE SURFACE TENSIONS OF AQUEOUS SOLUTIONS OF (a) SODIUM AND POTASSIUM CHLORIDES, (b) SODIUM CHLORIDE AND HYDROCHLORIC ACID.

By J. W. BELTON.

Received 7th June, 1935.

The addition of an electrolyte to water usually produces an increase in surface tension which is given by the relation

$$\gamma - \gamma_0 = km, \quad (1)$$

where γ and γ_0 are the surface tensions of the solution and of water respectively, k is a constant, and m is the number of moles of solute present per 1000 gms. of water. When two electrolytes are present the change in surface tension is usually taken as equal to the sum of the changes each would produce separately, and is given by

$$\gamma_{12} - \gamma_0 = k_1 m_1 + k_2 m_2, \quad (2)$$

where γ_{12} is the surface tension of the solution and the subscripts 1 and 2 refer to the two solutes. This relation may be conveniently tested by keeping the concentration of one solute constant and varying that of the other. A plot of γ_{12} against m should give

$$\left(\frac{\partial \gamma_{12}}{\partial m_1} \right)_{m_2} = k_1. \quad (3)$$

$$\left(\frac{\partial \gamma_{12}}{\partial m_2} \right)_{m_1} = k_2. \quad (4)$$

These considerations are applied below to solutions of sodium and potassium chlorides and of hydrochloric acid and sodium chloride.

Experimental.

The surface tensions of the solutions were obtained by the maximum bubble pressure method, the apparatus used being similar to that of Brown¹ to which reference should be made for complete details. Dry air was stored under pressure in a reservoir over mercury and was allowed to pass slowly over phosphorus pentoxide, through a glass wool trap, through a finely adjustable valve and into the experimental cell (Fig. 1) at A, and thence via B to a large reservoir kept at constant temperature. C was connected with a reservoir of butyl phthalate, the level of which could be easily changed, thus giving a fine adjustment of the level of the liquid in the cell. The cell at A and B was also in communication with the limbs of a manometer containing butyl phthalate, by means of which the pressure required to force a single bubble through the surface of the liquid could be measured with a cathetometer placed at a suitable distance. Both cell and manometer were kept in a thermostat at 25° (± 0.02). At

¹ *Phil. Mag.*, 1932, 13, 578.

each measurement the jet was arranged to be just coincident with the surface of the liquid, and when the bubble had passed through the surface the contact was broken. Some difficulty was experienced in the cleaning of the cell and jet. Before each fresh solution was examined, it was washed out with hot chromic acid and then with a large quantity of water; steam was then blown into it for about five minutes and finally it was dried by evacuation at 100°. The jet was made by drawing down a piece of quill tubing, breaking off at the constricted part and examining under a microscope until one satisfactory was obtained.

The surface tension was calculated from

$$\gamma = \frac{rg}{2} \left(h\rho - \frac{2}{3}r\rho_1 \right) \quad (5)$$

where r is the radius of the jet = 0.0102 cm.

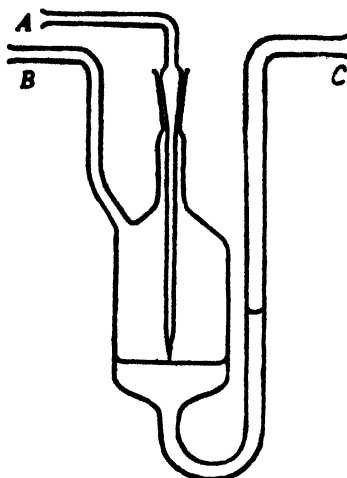


FIG. 1.

$g = 981$ cm./sec.²

h = maximum bubble pressure in cm. butyl phthalate.

ρ = density of butyl phthalate at 25° = 1.0434 gms./c.c.

ρ_1 = density of liquid under observation, found by a Westphal balance.

The surface tension in dyne/cm. of pure water found in this way was 72.01 at 25°, and that of pure benzene at the same temperature 28.20. These values are in good agreement with those generally accepted.

Binary Solutions.

The results obtained for binary solutions containing sodium chloride, potassium chloride and hydrochloric acid are given in Table I. The final column gives the value of the constant, k , calculated from equation (1). The surface tensions of hydrochloric acid solutions decrease with increasing concentration, while those of sodium and potassium chlorides increase.

TABLE I.—SURFACE TENSIONS OF BINARY SOLUTIONS.

	m .	h .	γ .	$\Delta\gamma$.	k .
Sodium Chloride Solutions	1.021	14.15	73.84	1.75	1.73
	2.080	14.48	75.59	3.58	1.72
	3.197	14.84	77.44	5.43	1.70
	4.360	15.22	79.43	7.42	1.70
	5.608	15.62	81.54	9.53	1.70
Potassium Chloride Solutions	1.000	14.12	73.68	1.67	1.67
	2.010	14.43	75.34	3.33	1.65
	3.051	14.70	76.73	4.72	1.55
	4.015	14.96	78.14	6.13	1.53
Hydrochloric Acid Solutions.	1.00	13.77	71.87	-0.14	-0.14
	3.00	13.73	71.64	-0.37	-0.12
	5.00	13.68	71.43	-0.58	-0.11

Ternary Solutions.

(a) **Aqueous Solutions of Sodium Chloride and Potassium Chloride.**—The mixtures were made up by weight from B.D.H. AR. chemicals and pure water of surface tension 72.01 dynes/cm. The surface tensions measured are given in Table II, together with the molal concentrations of the salts. The fifth and sixth columns give ($\gamma_{12} - \gamma_0$) observed, and calculated from (2). The agreement is good, but there is a discrepancy which is greater than the experimental error.

TABLE II.—SOLUTIONS OF SODIUM AND POTASSIUM CHLORIDES.

m_1	m_2	h	γ_{12}	$\Delta\gamma_{12}$ obs.	$\Delta\gamma_{12}$ calc.
1.01	1.05	14.435	75.35	3.34	3.55
1.01	2.07	14.735	76.91	4.90	5.24
1.01	3.09	15.015	78.37	6.36	6.51
1.01	4.12	15.24	79.54	7.53	8.09
2.02	1.00	14.725	76.86	4.85	5.15
2.02	2.01	14.98	78.46	6.45	6.81
2.02	3.00	15.26	79.97	7.96	8.03
3.01	1.01	15.05	78.55	6.54	6.80
3.01	2.01	15.39	80.15	8.34	8.44
3.00	3.00	15.62	81.54	9.53	9.67
4.02	1.00	15.38	80.30	8.29	8.50
4.02	2.01	15.72	82.08	10.07	10.17

Plots of γ_{12} against m for constant sodium chloride concentration and increasing potassium chloride, and for constant potassium chloride and increasing sodium chloride gave a series of nearly parallel straight lines. According to equations (3) and (4) a series of parallel straight lines should be obtained on both graphs, of slope h_2 and h_1 . The slopes (h'_1 and h'_2) for the various mixtures are given in Table III.; these values should be compared with those given in Table I, for sodium and potassium chloride alone. The curves for the mixtures with one component constant appear

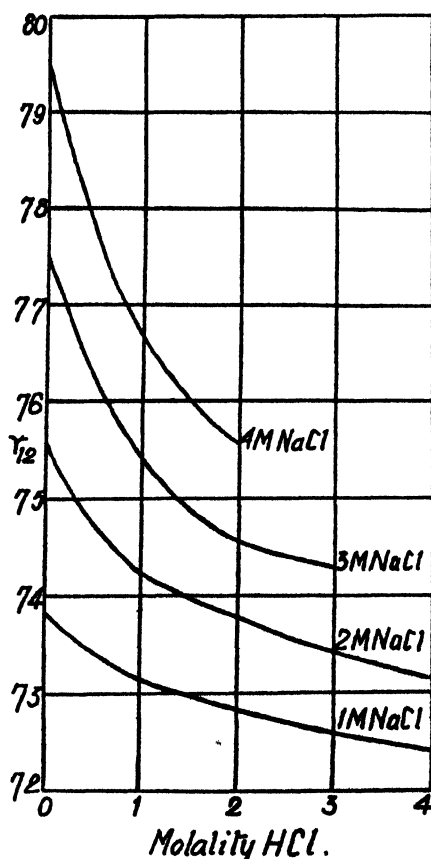
TABLE III.—SOLUTIONS OF SODIUM AND POTASSIUM CHLORIDES.

$m_2 = 1.$			$m_2 = 2.$			$m_2 = 3.$		
m_1	$\Delta\gamma$	h'_1	m_1	$\Delta\gamma$	h'_1	m_1	$\Delta\gamma$	h'_1
1	1.67	1.67	1	1.81	1.81	1	1.64	1.64
2	3.18	1.59	2	3.36	1.68	2	3.24	1.62
3	4.87	1.62	3	5.05	1.68	3	4.81	1.61
4	6.62	1.65	4	6.98	1.75		Mean	1.62
	Mean	1.63		Mean	1.73			

$m_1 = 1.$			$m_1 = 2.$			$m_1 = 3.$		
m_2	$\Delta\gamma$	h'_2	m_2	$\Delta\gamma$	h'_2	m_2	$\Delta\gamma$	h'_2
1	1.61	1.61	1	1.41	1.41	1	1.44	1.44
2	3.17	1.59	2	3.01	1.50	2	3.04	1.52
3	4.63	1.54	3	4.52	1.51	3	4.43	1.48
	Mean	1.57		Mean	1.50		Mean	1.48

TABLE IV.—SOLUTIONS OF SODIUM CHLORIDE AND HYDROCHLORIC ACID.

m_1 .	m_2 .	h .	γ_{12} .	$\Delta\gamma_{12}$.	$\Delta\gamma_{12}$ calc. from (2).	$\Delta\gamma_{12}$ calc. from (6).
0.99	1.0	14.01	73.12	1.11	1.63	1.13
1.98	1.0	14.22	74.23	2.22	3.27	2.28
2.95	1.0	14.45	75.42	3.41	4.87	3.40
3.98	1.0	14.69	76.68	4.67	6.63	4.64
4.96	1.0	14.86	77.57	5.56	8.29	5.81
1.06	2.0	13.96	72.86	0.85	1.64	0.89
2.00	2.0	14.14	73.78	1.77	3.16	1.75
3.01	2.0	14.31	74.68	2.67	4.84	2.72
4.00	2.0	14.47	75.54	3.53	6.55	3.83
1.00	3.0	13.91	72.59	0.58	1.44	0.57
2.01	3.0	14.07	73.43	1.42	3.10	1.36
3.02	3.0	14.23	74.28	2.27	4.76	2.12
0.99	4.0	13.88	72.43	0.42	1.29	0.30
1.99	4.0	14.02	73.15	1.14	2.95	0.96
1.00	5.0	13.84	72.26	0.25	1.24	0.12

FIG. 2.—Plot of Molality HCl — γ_{12} for NaCl — HCl mixtures.

to be slightly less steep than those with one component alone, although in one case they are equally steep (NaCl in 2MKCl). The contribution of each solute to the surface tension is thus a little less than it would have been in a separate solution.

(b) **Aqueous Solutions of Sodium Chloride and Hydrochloric Acid.**—The solutions were made up by weight from pure chemicals and the same water as before. The strength of the hydrochloric acid was verified by standardisation. Table IV. gives the molal concentrations of sodium chloride (m_1) and hydrochloric acid (m_2) and the corresponding surface tension. The fifth and sixth columns give the surface tension increments observed and calculated from (2). Comparison of these shows that the simple additive relation is only very approximate and that the discrepancies are much greater than those obtained for solutions of sodium and potassium chlorides. The plot of γ_{12} against m_1 (m_2 constant) gives a series of straight lines, but they are not parallel as would be expected from (3); the plot of γ_{12} against m_2 (m_1 constant) gives a series of curves again showing no agreement with (4) (Fig. 2). Examination of the data showed

that γ_{12} could be represented by the relation

$$\gamma_{12} - \gamma_0 = k_1 m_1 + k_2 m_2 + k_3 m_1 m_2^{\frac{1}{2}} \quad (6)$$

in which k_3 is an empirical constant equal to -0.5 . The values of $\Delta\gamma_{12}$, so calculated are given in the final column of Table IV. The agreement with the observed values is very good—a difference of one in the first place represents an error in the surface tension of one in seven hundred. The slopes of the curves for γ_{12} against m_1 (m_2 constant) and γ_{12} against m_2 (m_1 constant) are thus given by

$$\left(\frac{\partial \gamma_{12}}{\partial m_1}\right)_{m_2} = k_1 + k_3 m_2^{\frac{1}{2}} \quad \left(\frac{\partial \gamma_{12}}{\partial m_2}\right)_{m_1} = k_2 + \frac{1}{2} k_3 m_1 m_2^{-\frac{1}{2}} \quad (7)$$

Application of the Gibbs Equation.

The values of $(\partial \gamma_{12} / \partial m_1)_{m_2}$ and $(\partial \gamma_{12} / \partial m_2)_{m_1}$, which are calculable from (2) and from (6), may also be derived from the Gibbs equation, according to which

$$d\gamma = -\Gamma_1 d\mu_1 - \Gamma_2 d\mu_2 - \Gamma_3 d\mu_3 \quad (8)$$

where Γ_1 , Γ_2 , Γ_3 are the surface concentrations of the components and μ_1 , μ_2 , μ_3 their chemical potentials. If the surface is chosen so that $\Gamma_3 = 0$, then

$$\begin{aligned} d\gamma &= -\Gamma_1 d\mu_1 - \Gamma_2 d\mu_2 \\ &= -\Gamma_1 2RT \, d \log f_1 m_1 - \Gamma_2 2RT \, d \log f_2 m_2 \end{aligned} \quad (9)$$

where f_1 and f_2 are the appropriate activity coefficients of the solutes. If the concentration of one is kept constant and the other varied, then this may be written

$$-\frac{1}{2RT} \left(\frac{\partial \gamma_{12}}{\partial m_1}\right)_{m_2} = \Gamma_1 \left(\frac{1}{m_1} + \left(\frac{\partial \log f_1}{\partial m_1}\right)_{m_2}\right) + \Gamma_2 \left(\frac{\partial \log f_2}{\partial m_1}\right)_{m_2} \quad (10)$$

$$-\frac{1}{2RT} \left(\frac{\partial \gamma_{12}}{\partial m_2}\right)_{m_1} = \Gamma_2 \left(\frac{1}{m_2} + \left(\frac{\partial \log f_2}{\partial m_2}\right)_{m_1}\right) + \Gamma_1 \left(\frac{\partial \log f_1}{\partial m_2}\right)_{m_1} \quad (11)$$

For only one solute (subscript 0)

$$-\frac{1}{2RT} \frac{d\gamma}{dm} = -\frac{k}{2RT} = {}^0\Gamma \left(\frac{1}{m} + \frac{d \log f}{dm}\right) \quad (12)$$

Equations (3) and (4) and consequently (2) are thus special cases of a more general equation. A complete solution of equations (10) and (11) requires a knowledge of the variations of the activity coefficient of each component of the system, data not usually available. In certain cases, as below, approximations may be made and the adsorptions calculated.

(a) Aqueous Solutions of Sodium and Potassium Chlorides.

It may be assumed for this system that $(\partial \log f_1 / \partial m_1)_{m_2} = d \log f_1 / dm_1$. Combining (10) and (12), and (11) and (12) and putting k_1 for the slope in the mixed solution, we have

$$-\frac{k'_1}{2RT} = -\frac{\Gamma_1}{{}^0\Gamma_1} \cdot \frac{k_1}{2RT} + \Gamma_2 \left(\frac{\partial \log f_2}{\partial m_1}\right)_{m_2} \quad (13)$$

$$-\frac{k'_2}{2RT} = -\frac{\Gamma_2}{{}^0\Gamma_2} \cdot \frac{k_2}{2RT} + \Gamma_1 \left(\frac{\partial \log f_1}{\partial m_2}\right)_{m_1} \quad (14)$$

For the lower concentrations the $\partial \log f / \partial m$ terms are small and may be neglected. Hence

$$\Gamma_1 = \frac{k'_1}{k_1} \Gamma_1 \quad (15)$$

Even for 5*M* solutions the error introduced is only a few per cent. Similarly.

$$\Gamma_2 = \frac{k'_2}{k_2} \Gamma_2 \quad (16)$$

The approximate values of Γ_1 and Γ_2 calculated in this way are given in Table V. The sum $\Gamma_1 + \Gamma_2$ gives the total negative adsorption at the surface. The values of ${}_0\Gamma_1 + {}_0\Gamma_2$ for separate solutions, given for comparison, have been calculated from (12), the values of $d \log f / dm$ being obtained from the empirical equations of Harned.²

It appears that for this system each solute is hardly affected by the presence of the other, and that each is adsorbed to the same extent in the mixed solution as it would be in a separate solution. If the layer of water at the surface is assumed to be unimolecular, its thickness, δ , is given by 1000 $(\Gamma_1 + \Gamma_2) / (m_1 + m_2)$. These values are given in the final column of Table V. and the result, as for separate solutions of sodium and potassium chlorides, is about the diameter of a water molecule, with a tendency to become less at higher concentrations, probably due to a change in orientation.

TABLE V.—SOLUTIONS OF SODIUM AND POTASSIUM CHLORIDES.

m_1	m_2	Γ_1	Γ_2	$\Gamma_1 + \Gamma_2$	${}_0\Gamma_1 + {}_0\Gamma_2$	$\delta(\text{\AA}^\circ)$
1	1	0.39	0.35	0.74	0.79	3.7
1	2	0.41	0.65	1.06	1.10	3.5
1	3	0.38	0.89	1.27	1.29	3.2
1	4	0.38	1.07	1.45	1.46	2.9
2	1	0.60	0.34	0.94	1.01	3.1
2	2	0.63	0.63	1.26	1.32	3.1
2	3	0.59	0.85	1.44	1.51	2.9
3	1	0.78	0.34	1.12	1.19	2.8
3	2	0.82	0.62	1.44	1.50	2.9
3	3	0.77	0.83	1.60	1.69	2.7
4	1	0.92	0.34	1.26	1.34	2.5
4	2	0.97	0.62	1.59	1.64	2.6

Γ in moles/sq. cm. $\times 10^{10}$.

(b) Aqueous Solutions of Sodium Chloride and Hydrochloric Acid.

For this system $\partial \log f_2 / \partial m_1$ may be computed, but not $\partial \log f_1 / \partial m_2$. In order, then, to calculate either Γ_1 or Γ_2 the other must be known. Now it appears that the relative values of the terms in (10), calculated below, are such that changes in Γ_2 may be neglected. It may thus be assumed that $\Gamma_2 = {}_0\Gamma_2$ and Γ_1 calculated. A very large change in Γ_2 would be required to produce only a small error in Γ_1 calculated in this way. Further it must be assumed that $d \log f / dm$ is the same in both mixed and separate solutions; this will introduce a small error.

² *J. Amer. Chem. Soc.*, 1920, 42, 1808; 1922, 44, 252.

Equation (10) may now be written (using (7) and (12))

$$-\frac{1}{2RT}(k_1 + k_2 m_2^{\frac{1}{2}}) = -\frac{k_1}{2RT} \cdot \frac{\Gamma_1}{\delta \Gamma_1} + \Gamma_2 \left(\frac{\partial \log f_2}{\partial m_1} \right)_{m_2},$$

or

$$1 + \frac{k_2 m_2^{\frac{1}{2}}}{k_1} + \Gamma_2 \frac{2RT}{k_1} \cdot \left(\frac{\partial \log f_2}{\partial m_1} \right)_{m_2} = \frac{\Gamma_1}{\delta \Gamma_1}. \quad (18)$$

The values of k_1 (taken as 1.7) and k_2 are known, Γ_2 is put equal to $\delta \Gamma_2$ calculated from the data in Table I. The values of $(\partial \log f_2 / \partial m_1)_{m_2}$ were calculated from the data of Hawkins³ who found for mixtures of sodium chloride and hydrochloric acid up to total concentrations of 6M

$$\log f = -\frac{0.354\sqrt{2C_T}}{1 + A\sqrt{2C_T}} + B(2C_1) + B'(2C_T - 2C_1) - \log(1 - 0.002wm_T),$$

where C_T is the total molar concentration, C_1 the molar acid concentration, and A , B and B' are determined constants. The values of $\Gamma_1/\delta \Gamma_1$ calculated in this way are given in Table VI. The term involving Γ_2 is quite small throughout.

TABLE VI.—SOLUTIONS OF SODIUM CHLORIDE AND HYDROCHLORIC ACID.

m_1	m_2	Γ_1	$\left(\frac{\partial \log f_2}{\partial m_1} \right)_{m_2}$	$\frac{\Gamma_1}{\delta \Gamma_1}$	$\delta \delta$	δ_{12}
1	1	2.44×10^{-12}	0.0646	0.72	4.1	3.0
2	1	2.44×10^{-12}	0.0697	0.72	3.2	2.3
3	1	2.44×10^{-12}	0.0689	0.72	2.7	1.9
4	1	2.44×10^{-12}	0.0662	0.72	2.4	1.7
5	1	2.44×10^{-12}	0.0627	0.72	2.1	1.5
1	2	3.48×10^{-12}	0.0755	0.60	4.1	2.4
2	2	3.48×10^{-12}	0.0745	0.60	3.2	1.9
3	2	3.48×10^{-12}	0.0714	0.60	2.7	1.6
4	2	3.48×10^{-12}	0.0679	0.60	2.4	1.4
1	3	3.86×10^{-12}	0.0799	0.51	4.1	2.1
2	3	3.86×10^{-12}	0.0769	0.51	3.2	1.6
3	3	3.86×10^{-12}	0.0728	0.51	2.7	1.4
1	4	4.25×10^{-12}	0.0826	0.44	4.1	1.8
2	4	4.25×10^{-12}	0.0783	0.44	3.2	1.4
1	5	4.14×10^{-12}	0.0838	0.37	4.1	1.5

The thickness of the adsorbed water layer, assuming it to be uni-molecular, is given under $\delta \delta$ for the corresponding pure sodium chloride solution, and in the last column under δ_{12} for the mixtures ($\delta = 1000l/m$). The effect of the addition of hydrochloric acid is to reduce the thickness of this layer. The increased adsorption of HCl molecules seems to displace water molecules from the surface. An increase in the concentration of sodium chloride reduces the thickness of the water layer, but HCl is more effective than NaCl.

Summary.

The surface tensions of aqueous solutions of sodium and potassium chlorides, and of sodium chloride and hydrochloric acid, have been measured. The variation of the surface tension with the concentration of each component is discussed, and the surface adsorption of water calculated by means of the Gibbs equation.

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³ *J. Amer. Chem. Soc.*, 1932, **54**, 4480.

THE SURFACE TENSIONS OF TERNARY SOLUTIONS. PART II. THE SURFACE TENSIONS OF (a) ETHYL ALCOHOL-WATER-SALT MIXTURES (b) ACETIC ACID-WATER-SALT MIXTURES.

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In Part I. the surface tensions of solutions containing two electrolytes were investigated. These measurements are extended here to solutions containing an electrolyte and a non-electrolyte. The change in surface tension produced by the two electrolytes was shown to be very approximately equal to the sum of the changes each would have produced separately. For solutions containing non-electrolytes, which reduce the surface tension, and salts, which raise it, this additive relation does not apply even approximately; the resulting change may in some cases not even lie between the separately produced changes. No simple empirical equation connecting the surface tension and concentration can be applied to such mixtures.

The surface tension of an aqueous salt solution is given by

$$\gamma - \gamma_0 = km, \quad (1)$$

where γ_0 is the surface tension of water, k a constant, and m the molal concentration of the salt. The amount of water adsorbed at the surface may be found from the Gibbs equation—

$$-\frac{1}{2RT} \frac{d\gamma}{dm} = {}_0\Gamma \left(\frac{1}{m} + \frac{d \log f}{dm} \right) \quad (2)$$

in which f is the activity coefficient of the salt and ${}_0\Gamma$ its negative adsorption. When a non-electrolyte is added to the system this simple relation does not apply, but becomes, when the surface concentration of one of the components is put equal to zero,

$$\begin{aligned} d\gamma &= -\Gamma_1 d\mu_1 - \Gamma_2 d\mu_2 \\ &= -\Gamma_1 2RT d \log f_1 m_1 - \Gamma_2 RT d \log f_2 m_2, \end{aligned} \quad (3)$$

where μ_1 and μ_2 are the chemical potentials, f_1 and f_2 the activity coefficients of electrolyte and non-electrolyte respectively. If the concentration of the non-electrolyte is kept constant, this may be written

$$-\left(\frac{\partial \gamma}{\partial m_1} \right)_{m_2} = 2RT\Gamma_1 \left(\frac{1}{m_1} + \left(\frac{\partial \log f_1}{\partial m_1} \right)_{m_2} \right) + RT\Gamma_2 \left(\frac{\partial \log f_2}{\partial m_1} \right)_{m_2} \quad (4)$$

If the activity of the salt is unaffected by the non-electrolyte (1), (2) and (4) may be combined to give

$$\left(\frac{\partial \gamma}{\partial m_1} \right)_{m_2} = k_1 \frac{\Gamma_1}{{}_0\Gamma_1} - RT\Gamma_2 \left(\frac{\partial \log f_2}{\partial m_1} \right)_{m_2} \quad (5)$$

In order to calculate Γ_1 , Γ_2 and the activity coefficient of the non-electrolyte in presence of salt must be known. This equation is applied below to ethyl alcohol-water-salt and acetic acid-water-salt systems.

(a) Ethyl Alcohol-Water-Salt Mixtures.

The surface tensions were determined as in Part I. In all cases solutions were made up by weight from a stock solution of purified aqueous alcohol (moles alcohol per cent. = 2.03 from density measurements; $\gamma = 55.61$ dynes/cm.) and B.D.H. A.R. salts, which were further treated for the removal of water when necessary.

The results are given in Table I. which contains the molal salt concentration (m_1), the surface tension of the solution (γ) and the slope of the graph of γ against m_1 between each determined value of γ . The plot of γ against m_1 is given in Fig. 1. In contrast to the addition of salts to pure water, the surface tension is in all cases lowered. For most salts it falls off roughly linearly with concentration up to 2-3 *M.*, but the slope decreases at higher concentrations, and becomes constant in the case of potassium thiocyanate. A definite minimum point is shown by lithium chloride and ammonium chloride at fairly high concentrations.

The values at higher concentrations are more difficult to determine, and are more liable to experimental error; there is, further, the possibility of the accidental introduction of water which would cause an increase in the surface tension. The errors from these sources are, however, comparatively small.

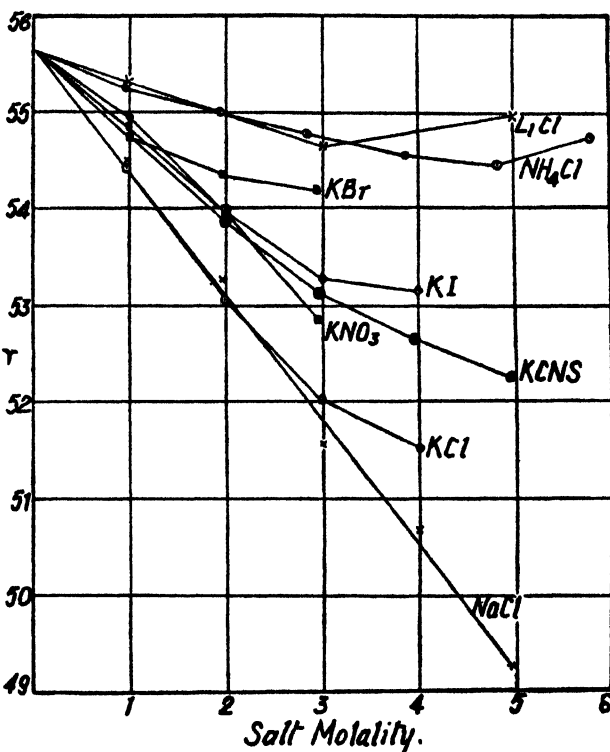


FIG. 1.—Plot of Salt Molality- γ for Ethyl Alcohol-Water-Salt Mixtures.

In order to apply equation (5) the activity coefficient of alcohol in the presence of salts must be known. Shaw and Butler¹ and Butler and Thomson² have found from vapour pressure measurements that for dilute ethyl alcohol-water mixtures the activity coefficient of the alcohol, when lithium chloride is added, is given by

$$f_2 = 1 + \kappa m_1,$$

¹ Shaw and Butler, *Proc. Roy. Soc.*, 1930, 129A, 519.

² Butler and Thomson, *Proc. Roy. Soc.*, 1933, 141A, 86.

TABLE I.

Salt.	m_1 .	γ .	$-\partial\gamma/\partial m_1$.	Salt.	m_1 .	γ .	$-\partial\gamma/\partial m_1$.
NaCl	0.998	54.50	1.11	NH ₄ Cl	0.97	55.24	0.37
	1.956	53.27	1.23		1.93	55.00	0.24
	2.99	51.57	1.70		2.83	54.77	0.23
	3.98	50.16	1.41		3.87	54.54	0.23
	4.97	49.27	0.89		4.83	54.44	0.10
KCl	0.99	54.45	1.16		5.80	54.72	-0.28
	1.99	53.08	1.37	KCNS	0.99	54.72	0.89
	2.98	52.01	1.07		1.98	53.86	0.86
	3.97	51.51	0.50		2.96	53.12	0.74
KI	0.99	54.97	0.64		3.95	52.64	0.48
	1.99	53.96	1.01		4.94	52.24	0.40
	2.98	53.28	0.58		9.87	51.71	0.11
	3.98	53.15	0.13		14.8	52.43	-0.14
K ₂ SO ₄	0.50	53.66	3.9		19.7	52.93	-0.10
KNO ₃	0.97	54.87	0.74	LiCl	1	55.31	0.30
	1.97	53.96	0.91		3	54.65	0.33
	2.96	52.85	1.11		5	54.95	-0.15
KBr	0.99	54.75	0.86				
	1.97	54.35	0.40				
	2.95	54.19	0.16				
KClO ₄	0.49	54.96	1.3				

which gives

$$\left(\frac{\partial \log f_2}{\partial m_1}\right)_{m_1} = \frac{\kappa}{f_2},$$

which is practically equal to κ in reasonably dilute solutions. Other salts would be expected to behave in a similar manner. The activity coefficient of a non-electrolyte in a salt solution is given by the equation of Debye and McAulay,³ according to which

$$\log f = \alpha n' \frac{\sum \nu_i z_i^2}{\nu} \cdot \frac{\epsilon^2}{2D_0 b k T},$$

where α is defined by the relation $D_m = D_0(1 - \alpha n)$, D_m is the dielectric constant of the non-electrolyte solution containing n molecules per c.c., D_0 is the dielectric constant of the solvent, n' the number of molecules of electrolyte per c.c., ν the number of ions given by the dissociation of one salt molecule, ν_i the number of ions of the i^{th} sort of valency z_i given by the dissociation of one salt molecule, e the electronic charge, b the mean ionic radius defined by $\sum \frac{\nu_i z_i^2}{b_i} = \frac{\sum \nu_i z_i^2}{b}$, and k the gas constant per molecule. This relation gives values which agree with those found experimentally for dilute solutions; κ may thus be calculated and values of $(\partial \log f_2 / \partial m_1)_{m_1}$ deduced for higher concentrations. These are given in Table II. The value of κ from the experimental data for lithium chloride is 0.186, while that calculated from Debye and McAulay's theory is 0.18.

³ Debye and McAulay, *Physik. Z.*, 1925, 26, 22.

Further, there is reason to believe that the surface adsorption of ethyl alcohol is independent of salt concentration. Butler and Lees ⁴ found this to be the case for the system referred to above and it is more likely to be true in the more dilute alcohol solution used here. The activity coefficient of the salt will be only affected slightly by the addition of so small a quantity of alcohol.

The type of experimental curve obtained when γ is plotted against m_1 is in agreement with equation (5). Its slope will depend on the relative values of $k_1\Gamma_{1/0}\Gamma_1$ and $RT\Gamma_2\kappa/f_2$; when these terms are equal the curve is parallel to the m_1 axis; at lower concentrations ($< 3M$) the second term must be much greater than the first. Table II. gives the values of $\Gamma_{1/0}\Gamma_1$ calculated from

$$\frac{\Gamma_1}{\Gamma_{1/0}} = \frac{1}{k_1} \left(\left(\frac{\partial \gamma}{\partial m_1} \right)_{m_2} + \frac{RT\Gamma_2\kappa}{f_2} \right).$$

TABLE II.

Salt.	m.	h_1 .	κ .	$\Gamma_{1/0}\Gamma_1$.	δ_0 .	δ' .
NaCl	0.5	1.73	0.20	0.40	4.2	1.7
	1.5	1.72		0.16	3.4	0.5
	2.5	1.70		-0.24	2.9	
	3.5	1.70		-0.12	2.5	
	4.5	1.70		0.12	2.2	0.3
KCl	0.5	1.67	0.24	0.81	3.8	3.1
	1.5	1.66		0.26	3.6	0.9
	2.5	1.53		0.28	3.1	0.9
	3.5	1.53		0.52	2.8	1.5
LiCl	0.5	1.56	0.18	0.83	3.0	2.5
	2	1.62		0.60	2.1	1.3
	4	1.67		0.70	1.4	1.0

Salt.	m.	h_1 .	κ .	$\Gamma_1/\theta\Gamma_1$.	Salt.	m.	h_1 .	κ .	$\Gamma_1/\theta\Gamma_1$.
KI	0.5	0.95	0.26	1.75	NH ₄ Cl	0.5	1.24	0.25	1.48
	1.5	0.95		0.94		1.5	1.24		1.26
	2.5	0.95		1.07		2.5	1.20		1.06
	3.5	0.94		1.35		3.5	1.15		0.93
						4.5	1.15		0.96
KBr	0.5	1.43	0.25	0.94	KNO ₃	5.5	1.12	1.23	
	1.5	1.43		0.98		0.5	1.09	0.19	0.88
	2.5	1.40		0.96					
	K ₂ SO ₄	0.25		2.74		0.59	0.44	2.5	1.00
KClO ₃			0.25		0.68			0.19	0.73

Γ_2 was taken as 4.0×10^{-10} moles/cm.², and the values of k_1 from the compilation in Rideal's "Surface Chemistry." The amount of water adsorbed is in some cases greater, in others less than for an aqueous salt solution of the same concentration. The value of $\Gamma_{1/0}\Gamma_1$ passes through a definite minimum for some of the salts examined. The thickness of

⁴ Butler and Lees, *J. Chem. Soc.*, 1932, 2097.

the aqueous layer (assuming it to be unimolecular) is given for a few salts in pure water (δ_0) and in aqueous alcohol (δ').

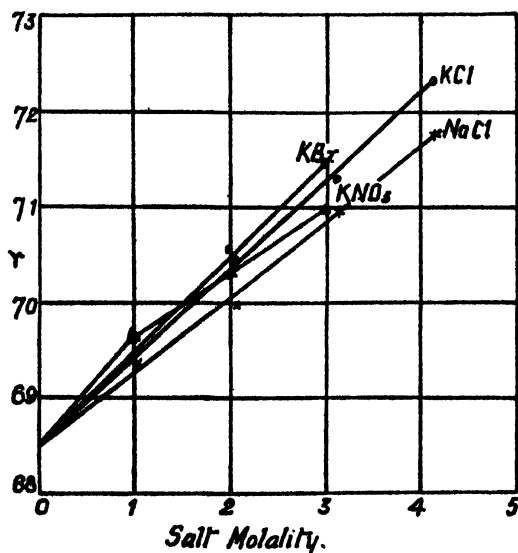


FIG. 2.—Plot of Salt Molality- γ for Acetic Acid-Water-Salt Mixtures.

TABLE III.

Salt.	m.	γ .	Salt.	m.	γ .
NaCl	1.021	69.36	KBr	1.00	69.65
	2.043	69.94		2.00	70.56
	3.064	70.92		3.00	71.44
	4.086	71.72	KNO ₃	1.00	69.65
KCl	1.018	69.49		2.00	70.32
	2.037	70.43		3.00	70.99
	3.056	71.30	K ₂ SO ₄	0.50	69.39
	4.074	72.31			

TABLE IV.

Salt.	m.	h_2 .	κ .	$\partial\gamma/\partial m$.	Γ_1/Γ_1 .
NaCl	1-4	1.7	0.065	0.79	0.68
KCl	1-4	1.6	0.026	0.93	0.68
KBr	1-3	1.4	0.014	0.99	0.76
KNO ₃	1	1.09	-0.021	1.16	0.95
	2	1.05	-0.021	0.92	0.76
	3	0.99	-0.021	0.83	0.72

(b) Acetic Acid-Water-Salt Mixtures.

The experimental procedure was identical with that previously adopted. The solutions were made up by weight from a stock acetic acid solution (0.353 moles per cent.) and the salts used were B.D.H. AR. grade. The measured surface tensions (γ) are given in Table III. in which m is the molal salt concentration; the plot of γ against m is given in Fig. 2.

It will be observed that the surface tension increases with increasing salt concentration as for pure water as solvent, and in contrast to ethyl alcohol-water mixtures in which it decreases. The addition of a small amount of acetic acid to an aqueous salt solution produces an effect opposite to that when a small amount of ethyl alcohol is added. A linear relation between γ and m holds for sodium chloride, potassium

chloride and potassium bromide as for pure water, while potassium nitrate gives a straight line in neither.

In order to apply equation (5) the activity coefficient of acetic acid must be known. These have been calculated for certain salts by Randall and Failey⁵ from the data of Sugden⁶ for the distribution of acetic acid between amyl alcohol and water. Randall and Failey found, further, that $\log f = \kappa m$, where κ is a constant dependent on the salt but independent of its concentration. Hence $(\partial \log f_2 / \partial m_1)_{m_2} = \kappa$. The values of κ are given in Table II.

There are grounds (*cf.* (a)) for believing that Γ_2 is independent of salt concentration and on this basis Γ_1/Γ_2 may be calculated. These values are given in Table IV.; $\partial \gamma / \partial m$ gives the smoothed values from the graphs in Fig. 2 and Γ_2 has been taken as 10^{-10} moles/sq. cm., the value corresponding to the acetic acid solution employed.

The changes in the water adsorption are not so great as those found for ethyl alcohol-water-salt mixtures, and, further, for sodium chloride, potassium chloride and potassium bromide, the value of Γ_1/Γ_2 is independent of salt concentration. The type of curve obtained experimentally—increasing surface tension with increasing salt concentration—thus agrees with the Gibbs equation if the water adsorption changes. Both systems described in (a) and (b), although they give very different results for the relation between salt concentration and surface tension, agree with the Gibbs equation if a change in the extent of water adsorption takes place.

Summary.

The surface tensions of ethyl alcohol-water-salt mixtures and of acetic acid-water-salt mixtures have been measured. The results are discussed in relation to the Gibbs equation and the surface adsorption of water calculated.

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⁵ Randall and Failey, *Chem. Rev.*, 1927, 4, 285.

⁶ Sugden, *J. Chem. Soc.*, 1926, 129, 177.

THE ACID-COMBINING CAPACITY OF WOOL.

BY J. B. SPEAKMAN AND E. STOTT.

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The swelling of wool fibres is much more pronounced in concentrated solutions of weak acids than in solutions of strong acids at the same p_H . For example, the increase in diameter of fibres on transference from distilled water to hydrochloric acid at p_H 0.6 is of the order of 3 per cent., whereas the increase in diameter in (mono)chloroacetic acid at the same p_H is 18 per cent.¹ In 98/100 per cent. formic acid, the diameter swelling may be as much² as 50 per cent. Since the pronounced lateral swelling which occurs in concentrated solutions of weak acids is accompanied by only a very small length contraction, it has been argued that

¹ Speakman and Stott, *Trans. Faraday Soc.*, 1934, 30, 539.

² Speakman, *Proc. Roy. Soc.*, 1931, 132A, 167.

the peptide chains of wool are bridged *in one plane* by cystine and salt linkages, as shown in Fig. 1.³

Such a structure would permit a pronounced increase in fibre diameter, without serious length contraction, if the sheets of covalently linked peptide chains are separated from one another against van der Waals attractive forces only. The heat of reaction of wool with concentrated solutions of weak acids should therefore be less than with solutions of strong acids having the same p_H . Further, determinations of the swelling and heat of reaction of wool fibres in solutions of weak and strong acids of varying p_H should permit the cohesion between the sheets of covalently linked peptide chains to be calculated. With such

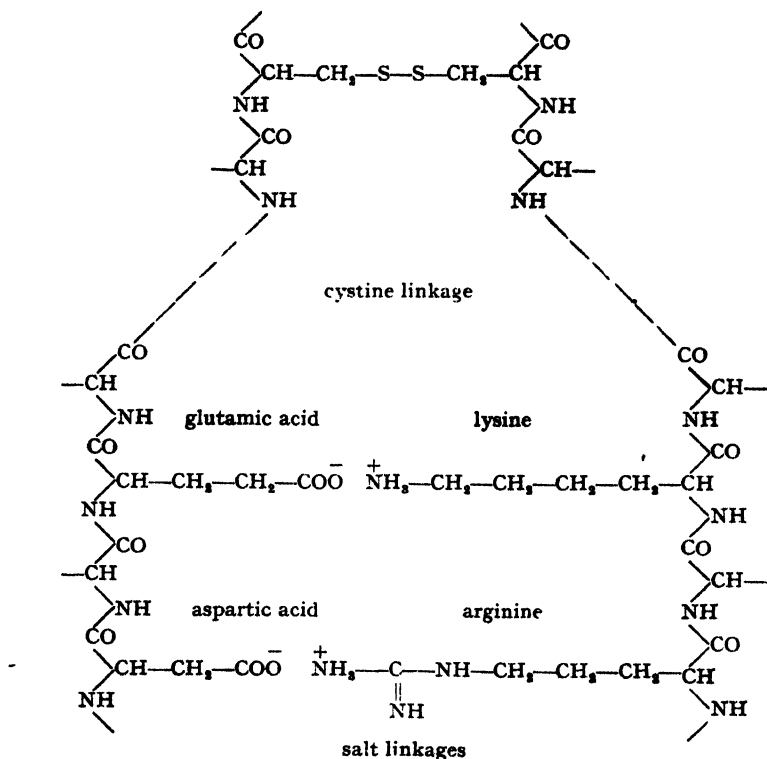


FIG. 1.

considerations in mind, the swelling of wool fibres was studied as a function of p_H with hydrochloric and chloracetic acid solutions, giving the results which have been reported in a previous paper.¹ Determinations of the corresponding heats of reaction were then undertaken. Contrary to the view outlined above, the heat of reaction with chloracetic acid solution at p_H 1 was found to be roughly twice that in hydrochloric acid at the same p_H . Such a result is difficult of explanation if Knecht,⁴ Meyer⁵ and Porai-Koschitz⁶ are correct in concluding that

³ Astbury and Woods, *Phil. Trans.*, 1933, 232, 333; Speakman, *J. Soc. Dyers and Colourists, Jubilee Number*, 1934, p. 43.

⁴ Knecht, *Ber.*, 1920, 53, 2164.

⁵ Meyer, *Mell. Textilberichte*, 1926, 7, 605.

⁶ Porai-Koschitz, *J. prakt. Chem.*, 1933, 137, 179.

the maximum acid-combining capacity of wool is the same for all acids and has a value of about 80 c.c. of $N/1$ acid per 100 g. wool. There are, however, difficulties in the way of accepting this conclusion. In the first place, the papers of Meyer and Porai-Koschitz contain errors of calculation. As regards the former, complete titration data are given for perchloric acid, and re-calculation from the data indicates a maximum acid-combining capacity of 42 and not 81 c.c. of $N/1$ acid per 100 g. wool. Similarly, Porai-Koschitz gives data for sulphuric acid which indicate an acid-combining capacity of 42.5 and not 81.1 c.c. of $N/1$ acid per 100 g. wool. In addition, Meyer studied the combination of wool with acids as a function of concentration and not of p_H , and since the p_H of solutions of weak acids changes but little with concentration, there can be no certainty that *maximum* acid combining capacity was measured in such cases. For reasons such as these, it was found necessary to study the combination of wool with hydrochloric and chloracetic acids as a function of the p_H of the solutions, so that the anomaly of a higher heat of reaction with the weak acid might be discussed and explained. Actually the titration curve for wool and hydrochloric acid is already well established,⁷ but it was considered desirable to carry out repeat experiments with the wool used for determinations of heats of reaction and swelling.

As a corollary to the main investigation, experiments were carried out with other acids because, although combination of wool with acids has been studied repeatedly as a function of concentration, there are no reliable data for combination as a function of p_H . Some years ago, Speakman⁸ utilised the data of Dietl,⁹ Fort and Lloyd,¹⁰ and Georgievics and Pollak¹¹—data for the amounts of different acids which combine with wool in solutions of varying concentration—to calculate the amounts of acid combined as a function of p_H in the case of hydrochloric, sulphuric, oxalic and phosphoric acids. Although only of an approximate nature, the resulting curves indicated that combination of acids and wool follows the same general rules as were found valid by Loeb¹² for proteins such as gelatin and casein, *i.e.*, if oxalic and phosphoric acids are regarded as being monobasic, the maximum acid-combining capacity is in both cases the same as for hydrochloric acid. Sulphuric acid was found to be neither monobasic nor dibasic in reaction with wool, in agreement with the data since obtained for the swelling of fibres in sulphuric acid solutions,¹ but the case of weak acids was not discussed. As already mentioned, these conclusions were drawn from calculations which were admittedly of an approximate character, and some doubt on their validity was thrown by Elöd's claim¹³ that between p_H 2.4 and 4.9 wool combines with twice as many equivalents of sulphuric acid as of hydrochloric acid, whereas between p_H 1.2 and 2.4 combination with the two acids seems to be identical. Such a result is in direct conflict with determinations of swelling in the two acids, as well as with Loeb's results for proteins in general. Apart from Elöd's work on sulphuric acid, the only attempt which has been made to study acid combination

⁷ Speakman and Hirst, *Trans. Faraday Soc.*, 1933, **29**, 148.

⁸ Speakman, *J. Soc. Dyers and Colourists*, 1924, **40**, 408.

⁹ Dietl, *Koll. Z.*, 1914, **14**, 319.

¹⁰ Fort and Lloyd, *J. Soc. Dyers and Colourists*, 1914, **30**, 5.

¹¹ Georgievics and Pollak, *Sitzungsber. der Kaiserl. Acad. der Wiss.*, 1911, **120** (2b), 465.

¹² Loeb, *Proteins and the Theory of Colloidal Behaviour*, 1922.

¹³ Elöd, *Trans. Faraday Soc.*, 1933, **29**, 327.

as a function of p_H seems to be that of Wilkinson and Tyler.¹⁴ Their data for sulphuric acid are not in agreement with those of Elöd, but their results, in general, suffer from the disadvantage of being incomplete and inconsistent, oxalic acid, for example, being found to combine with wool to a greater extent than phosphoric acid at the same p_H .

The purpose of the present investigation is therefore to determine the titration curves of wool with hydrochloric, chloracetic, sulphuric, oxalic and phosphoric acids in order (1) to establish the general laws governing combination with acid and (2) to discover whether the greater heat of reaction of wool with weak acids than with strong acids at the same p_H is to be referred to a higher combining capacity for weak acids. As regards the latter possibility no data are available.

Experimental.

The Cotswold wool chosen for experiment was in the form of "top." It was freed from oil and soap by successive extraction with alcohol and ether in a Soxhlet apparatus, adsorbed alcohol being afterwards removed by repeated washing in distilled water. The purified wool was then transferred to acid solution at about p_H 3.5 (78 g. wool to 4 litres of solution) in order to adjust the initial p_H of the wool to 4.8, the point at which combination with acid commences. Treatment with acid solution or distilled water was repeated until the p_H of the solution in equilibrium with the wool was 4.8, adjustment being carried out in all cases with the acid to be used in subsequent experiments. The wool was then removed, centrifuged and dried in an atmosphere maintained at 22.2° C. and 65 per cent. relative humidity. Once the wool had reached equilibrium with the air of the humidity room, 2-4 g. samples were weighed out in weighing bottles. Several of these samples were dried over phosphorus pentoxide for 14 days *in vacuo* in order to determine the percentage by weight of water adsorbed by the wool. The dry weights of the remaining samples were then calculated from the air-dry weights.

Determinations of acid-combining capacity were carried out in the following manner. A known dry weight of wool was immersed in 200 c.c. of the acid solution of known p_H at 22.2° C. (constant temperature room) for two days or more, the 8-oz. bottles containing the wool and solution being shaken intermittently. At the end of this time, the solution in equilibrium with the wool was withdrawn and its p_H was determined by means of the glass electrode. When the final p_H was greater than about 2.5, the amount of acid combined with the wool was calculated from the p_H measurements by reference to the p_H -normality curve obtained from the measurements of initial p_H . Below p_H 2.5, it was found to be more accurate to determine the amount of acid combined with the wool by titrating aliquots of the original and equilibrium solutions with caustic soda. In most cases, phenolphthalein was used as indicator, but phosphoric acid necessitated the use of a mixed indicator composed of 1 part of α -naphtholphthalein and 2 parts of phenolphthalein. The mixed-indicator titrations of phosphoric acid were also confirmed by titrations carried out in presence of silver nitrate, using methyl-red as indicator. With all acids, when the initial p_H was about 1, the change in concentration of the solutions during contact with wool was small. In consequence, to obtain reliable values for the amount of acid combined with wool at low p_H , the titrations were carried out in a constant temperature room, using the strictest possible technique. A possible source of error, peculiar to solutions of low p_H , arises from the fact that the samples of wool used for experiment (*vide supra*) were sometimes dry and sometimes contained 16.1 per cent. of water, although the dry weights were known in all cases.

¹⁴ Wilkinson and Tyler, *J. Soc. Dyers and Colourists*, 1928, 44, 241, 369.

Our attention was drawn to the matter by Mr. F. Townend, and parallel experiments carried out with the two types of wool in hydrochloric acid at p_H 0.51 indicated that the wet wool appeared to combine with more acid than the dry, owing to the fact that the adsorbed water diluted the acid to which the wool was added. When corrected for the dilution factor, the two results were almost identical: 76.9 and 74.9 c.c. $N/1$ acid combined with 100 g. dry wool. The lower value is that calculated from data for wool containing 16.1 per cent. water, the uncorrected combining capacity being 84.2 c.c. $N/1$ acid per 100 g. wool, and it seems possible that part of the water adsorbed by wool is too strongly combined to be available for dilution. In order to avoid any uncertainty in interpreting results, experiments with acid solutions of low p_H were therefore carried out with dry wool in all cases. At high p_H the error is insignificant and the two types of wool were used indiscriminately. Using the technique described above, the results summarised in Table I. were obtained.

TABLE I.

Acid.	Final p_H	C.c. $N/1$ Acid Combined with 100 g. Dry Wool.		Acid.	Final p_H	C.c. $N/1$ Acid Combined with 100 g. Dry Wool.	
		p_H	Titration.			p_H	Titration.
Hydrochloric acid	0.51	—	76.9	Oxalic acid	0.80	—	194.7
	0.62	—	79.7		1.03	—	174.6
	1.10	—	79.6		1.45	—	143.4
	1.41	—	74.7		1.50	—	146.4
	1.76	—	63.4		1.81	—	115.9
	2.41	33.0	—		1.83	—	114.5
	2.70	19.3	—		2.18	—	85.4
	2.72	20.2	—		2.36	—	71.2
	2.94	14.0	—		2.89	41.7	—
	3.38	4.6	—		3.29	26.3	—
	3.53	4.0	—		3.39	21.0	—
	4.33	0.5	—		3.57	15.8	—
Sulphuric acid	0.78	—	105.5	Phosphoric acid	1.13	—	243.1
	1.60	—	83.5		1.43	—	229.9
	1.86	—	78.8		1.64	—	198.4
	1.98	—	76.5		2.07	—	128.5
	2.39	—	63.5		2.19	—	110.9
	2.46	—	58.4		2.50	—	70.7
	2.92	44.8	—		2.90	28.1	—
	3.08	36.7	—		3.08	23.0	—
	3.32	29.2	—		3.43	11.1	—
	3.45	22.5	—		4.17	2.1	—
	3.84	11.4	—	Monochloroacetic acid	1.43	—	157.3
	3.86	13.6	—		1.54	—	122.2
	4.24	5.2	—		1.85	—	72.6
	4.50	2.2	—		2.01	—	59.8
	4.60	3.0	—		2.22	—	51.1
	4.67	1.1	—		2.54	26.7	—
	4.75	0.4	—		2.78	18.0	—
					3.28	6.1	—
					3.87	1.3	—
					4.55	0.6	—

Discussion of Results.

In discussing the results, which are illustrated in Fig. 2, it is important to note that the final p_H measured is that of the solution with which the wool was in equilibrium. The significant p_H is that within the fibres, and the difference between internal and external p_H , besides depending on p_H , varies with the basicity and strength of the acid under considera-

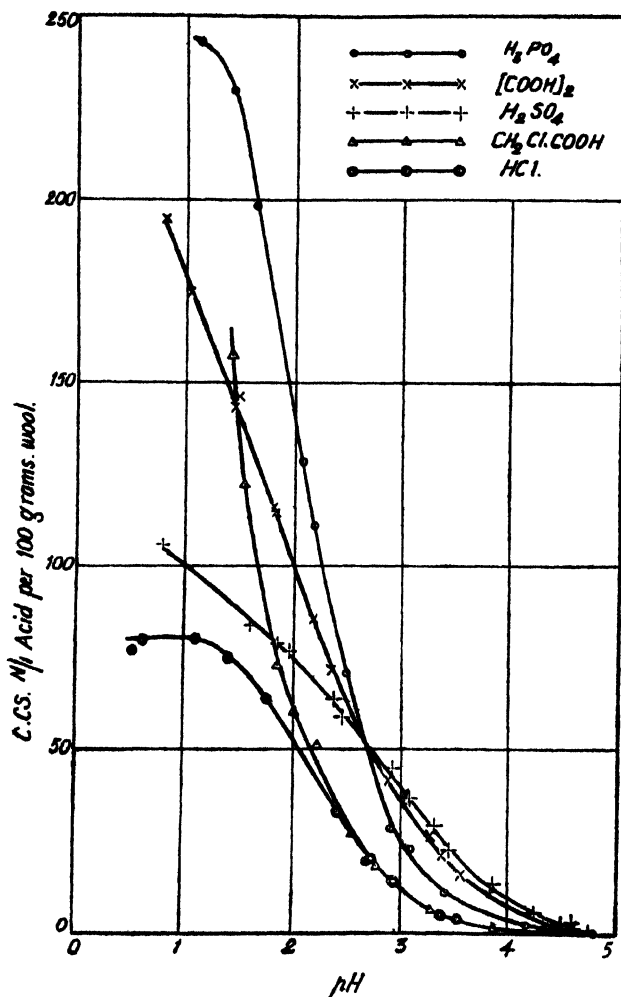


FIG. 2.

Elöd,¹² the amount combined with wool is throughout greater than with hydrochloric acid. In terms of the Procter-Wilson theory of swelling, the relative positions of the hydrochloric and sulphuric acid titration curves are in strict keeping with the swelling measurements recorded in a previous paper.¹

As regards the main purpose of this investigation, it is clear from

For this reason it is difficult to discuss the results in relation to those of Loeb for other proteins, except in the case of strongly acid solutions, where the p_H inside and outside the fibres are approximately the same. At p_H 1, however, phosphoric, oxalic and hydrochloric acids combine with wool in the approximate proportions, 3:2:1, and it is clear that phosphoric and oxalic acids are monobasic in reaction with wool. Sulphuric acid, which appears to behave as a monobasic acid at high p_H , tends to become dibasic at low p_H , although, contrary to the results of

Fig. 2 that monochloroacetic acid combines with wool to a far greater extent than hydrochloric acid in solutions of low p_H . This is no doubt the explanation of the fact that the heat of reaction between wool and chloroacetic acid is so much greater than with hydrochloric acid at p_H 1. Since, in addition, concentrated solutions of weak acids cause a far greater swelling of wool than strong acids, such as hydrochloric, it seems likely that the three phenomena are inter-related. As has already been indicated, fibre swelling is greater in weak acids than in strong because the swelling pressure developed in concentrated solutions of weak acids is great enough to separate the sheets of covalently linked peptide chains against cohesive forces. According to Astbury and Woods,⁸ the nature of the latter is illustrated in Fig. 3, where each peptide chain forms part of a separate sheet of covalently linked peptide chains.

So great is the stability of the arrangement that the peptide groups of an intact micelle can have little or no affinity for acid, but when the sheets of linked peptide chains are separated by swelling in weak acids, the $-NH-$ groups are freed for combination with acid. In other words, the increased heat of reaction and increased combining power of wool with weak acids are to be referred to the separation of sheets of linked peptide chains by swelling forces, with the release of

$-NH-$ groups for combination with acid. Similarly, the failure of Stiasny and Scotti¹⁵ to detect any difference between the simple peptides, from glycine to penta-glycyl glycine, in their affinity for hydrochloric acid, may be due to association of the peptide groups of paired molecules. On the other hand, it is doubtful whether Stiasny's experi-

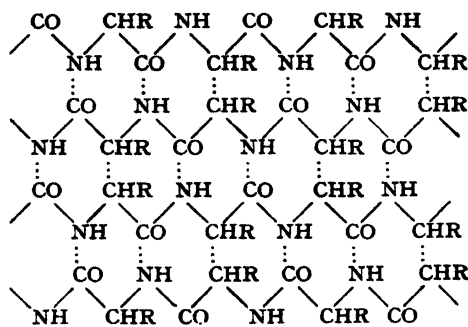


FIG. 3.

ments would be capable of detecting combination with $-NH-$ groups of the order of that observed with wool. In the latter case, combination of acid with $-NH-$ groups may have important consequences. At the surface of the wool fibre, for example, a number of $-NH-$ groups is always available for combination with acid, as may be seen by reference to Fig. 3. In consequence, the surface of the fibre has a greater affinity for acid than the interior, and methods of measuring the "isoelectric point" of wool which depend on surface properties will not be valid for the fibre as a whole. This may be the reason why Harris¹⁶ and Wilkerson,¹⁷ measuring the cataphoresis of particles of wool and hair, found values of 3.4 and 3.8, respectively, for the "isoelectric point" of wool and hair. Actually, the point at which wool begins to combine with acid is p_H 4.8, and in buffer solutions at p_H 3.4 it is combined with acid to the extent of one-third of its maximum acid-combining capacity,¹ so that determinations of the "isoelectric point" of wool by cataphoresis have no value in relation to the properties of the fibre as a whole.

In conclusion, it is evident that if the earlier measurements of the

¹⁵ Stiasny and Scotti, *Ber.*, 1930, **63**, 2977.

¹⁶ Harris, *Bur. Stand. J. Res.*, 1932, **8**, 779.

¹⁷ Wilkerson, *J. Biol. Chem.*, 1935, **109**, xcix.

swelling of wool fibres in hydrochloric and chloracetic acid solutions, together with the present determinations of acid-combining power in the same media, are combined with determinations of the heats of reaction in solutions of varying p_H , it should still be possible to calculate the cohesion between the sheets of covalently linked peptide chains which form the micelles of the wool fibre. We are indebted to the Government Grant Committee of the Royal Society for a grant in aid of the determination.

Summary.

The titration curves of wool with hydrochloric, monochloroacetic, sulphuric, oxalic and phosphoric acids, have been determined and show that oxalic and phosphoric acids are monobasic in reaction with wool. At high p_H , sulphuric acid is more nearly monobasic than dibasic, owing mainly to the distance separating the basic side-chains responsible for combination with acid. At low p_H , however, weak acids such as chloroacetic, combine with wool to a far greater extent than hydrochloric acid. Closely related to this phenomenon are the greater swelling and higher heat of reaction of wool in weak acids. It seems probable that the separation of sheets of covalently linked peptide chains, which occurs in concentrated solutions of weak acids owing to the great swelling pressure developed, frees the peptide linkages from mutual attraction and effectively liberates $-NH-$ groups for combination with acid. At the surface of the fibre some $-NH-$ groups are always available and, in consequence, cataphoretic determinations of the "isoelectric point" of wool are not valid for the fibre as a whole.

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ABSORPTION SPECTRA OF IODINE SOLUTIONS AND THE INFLUENCE OF THE SOLVENT.

BY O. J. WALKER.

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Introduction.

The broad classification of I_2 solutions into two groups according to their colour is confirmed by the absorption spectrum measurements of Groh,¹ and of Getman.² They showed that the wave-length of maximum absorption, λ_{max} , of the I_2 band in the visible region is, in the brown solutions, displaced about 70 $m\mu$ towards the U.V. relative to its value of about 520 $m\mu$ in the violet solutions. [Recently it has been shown³ that the substances ICl and IBr exhibit a similar type of dichroism in the same two classes of solvent, the displacement of λ_{max} being about 100 $m\mu$ in both cases.] The difference in the absorption spectra of violet and brown solutions of I_2 is thus well-marked, and can be

¹ Groh, *Z. anorg. Chem.*, 1927, 162, 287.

² Getman, *J. Amer. Chem. Soc.*, 1928, 50, 2883.

³ Gillam and Morton, *Proc. Roy. Soc.*, 1929, 124A, 604; Gillam, *Trans. Farad. Soc.*, 1933, 29, 1132.

ascribed to the chemical formation of solvates in the brown solutions, evidence for which is obtained by an examination of other properties of such solutions.⁴ The brown solutions, except when freshly prepared, usually also contain HI_2 (or I_3^- ions) as a result of substitution reactions between the I_2 and solvent molecules.⁵

Uncertainty still exists, however, as to the existence and magnitude of any solvent effect in many "violet" or "red" solutions of I_2 . For example, solutions in C_6H_6 are usually classified in the violet group, although they have a definite reddish tinge, and the absorption spectrum shows that λ_{max} is displaced about 10-20 $\mu\mu$ towards the U.V. as compared with its value for a solution in CCl_4 , which gives truly violet solutions. Some kind of interaction between the I_2 and C_6H_6 molecules is indicated. Further evidence for this was obtained from the work of Williams⁶ and of Müller and Sack,⁷ who found a value of about $1.0 - 1.2 \times 10^{-18}$ e.s.u. for the dipole moment of I_2 dissolved in C_6H_6 , but their work has been criticised recently by Wassiliew and co-workers,⁸ who showed that I_2 has no measurable dipole moment in this solvent. Hildebrand and Jenks,⁹ found that solutions of I_2 in C_6H_6 are abnormal in respect to their solubility-temperature relationship compared with other violet solutions. From similar considerations,¹⁰ it has been suggested that in solutions of I_2 in ethylene dibromide, in spite of their violet colour, there is also some approach to solvation. In the case of solutions in $\text{C}_2\text{H}_4\text{Br}_2$ the solvation may be attributed to the polar nature of the solvent ($\mu = 1.4 \times 10^{-18}$ e.s.u.). Benzene, on the other hand, is a solvent which has no resultant dipole moment. It seemed of interest, therefore, to examine further by means of absorption spectrum measurements the influence of the polar nature of the solvent molecules on the solvation of I_2 in different solvents. The effect of the polarity of the solvent in producing displacements of absorption bands of solutions has been studied by Scheibe¹¹ and others. In the case of violet solutions of I_2 it is not possible to draw any conclusions from the existing absorption spectrum data, because the measurements of different investigators do not extend over a large enough number of chemically similar solvents and frequently do not agree sufficiently for any one solvent. Absorption measurements have, therefore, been made of I_2 dissolved in a number of chloro-paraffins, since these solvents provide a fairly wide range of polarity and give solutions which show quite marked differences in colour.¹² During the course of this work a paper appeared by Chatelet¹³ on the absorption spectra of fairly concentrated solutions of I_2 in many of these solvents. In the present work very dilute solutions were used in order to minimise any effects due to interaction between the I_2 molecules themselves (*cf.* ref. 19). The solvents used were carbon tetrachloride, chloroform, methylene chloride, ethylene dichloride, *n*-propyl chloride, *n*-butyl chloride and *cis*- and *trans*-dichloroethylenes.

⁴ Gmelin-Kraut, *Handb. anorg. Chemie*, 8 Aufl., 1931, Jod, p. 125.

⁵ Cf. Batley, *Trans. Farad. Soc.*, 1928, **24**, 438.

⁶ Williams, *Physikal. Z.*, 1928, **29**, 174.

⁷ Müller and Sack, *Physikal. Z.*, 1930, **31**, 821.

⁸ Wassiliew, Syркин and Kenez, *Natura*, 1935, **135**, 71.

⁹ Hildebrand and Jenks, *J. Amer. Chem. Soc.*, 1920, **42**, 2180.

¹⁰ Negishi, Donnally and Hildebrand, *J. Amer. Chem. Soc.*, 1933, **55**, 4799.

¹¹ Scheibe, *Ber.*, 1925, **58**, 586; 1926, **59**, 2617.

¹² Kaufmann and Levite, *Ber.*, 1919, **52**, 619.

¹³ Chatelet, *Ann. Chim.*, 1934 (11), **2**, 5.

Experimental.

Materials.

Iodine.—A.R.I., containing no Cl, CN, etc., kept dry over CaCl_2 .

Solvents.—In most cases the purest B.D.H. product was further treated with H_2SO_4 , NaOH solution, H_2O , dried over CaCl_2 or P_2O_5 and distilled, neglecting the first and last fractions.¹⁴ The *cis*- and *trans*-isomers of $\text{C}_6\text{H}_5\text{Cl}_2$ were obtained by fractionation of the purified mixed product, using an efficient fractionating column. The fractions distilling between the limits given were used. The b.p. of the solvents, which agree well with those given in the literature, are as follows, with the corresponding barometer readings (in mm.): CCl_4 76.8° (762), CHCl_3 61.1–61.4 (762), CH_2Cl_2 40.1–40.3 (769), $\text{C}_6\text{H}_5\text{Cl}$ 83.2–83.3 (760), *n*- $\text{C}_6\text{H}_5\text{Cl}$ 46.5–47.0 (775), *n*- $\text{C}_6\text{H}_5\text{Cl}$ 77.9–78.3 (774), *cis*- $\text{C}_6\text{H}_5\text{Cl}_2$ 59.9–60.1 (760), *trans*- $\text{C}_6\text{H}_5\text{Cl}_2$ 48.4–49.4 (741).

The concentration of the solutions was 0.001 gm. mols./litre in every case. Three or more freshly prepared solutions were used for each solvent.

Absorption Measurements.

These were made by means of a Hilger-Nutting Spectrophotometer and Hilger wave-length spectrometer. The drum of the spectrometer was set at wave-lengths of 10 $m\mu$ intervals between 440–620 $m\mu$, and the photometer adjusted to equal intensities. The results were corrected for the zero of the instrument, which was checked at intervals. A 100 C.P. pointolite lamp was used as the source, and the solutions were placed in stoppered quartz cells, for which d (internal thickness) = 0.99 cm., a similar cell containing pure solvent being placed in the comparison beam. The room temperature during the measurements varied between 16° and 22°.

In this paper the molecular extinction coefficient (ϵ) is defined in the usual way by the expression

$$\epsilon cd = \log_{10} I_0/I$$

where I_0 = intensity of incident light.

I = " " transmitted light.

c = concentration of I_2 in gm.-mols./litre (0.001 M).

d = length of absorbing layer of solution (0.99 cm.).

As a check on the absolute values of the extinction coefficients the absorption curve of I_2 in CCl_4 was also determined, using a Hilger rotating sector photometer and photographic technique, and results in good agreement with those of the above method were obtained.

Results.

All the absorption bands are of the form shown in Fig. 1, in which only the curve for the solution in CCl_4 is reproduced, as the curves are too crowded together in a small scale diagram. The curves for the other solvents are all (except with *trans*- $\text{C}_6\text{H}_5\text{Cl}_2$) more or less displaced towards the violet end, but the intensity and width of the bands are constant within the limits of experimental error (except with the two $\text{C}_6\text{H}_5\text{Cl}_2$ isomers). This is brought out clearly by Table I., in which the three quantities characteristic of a simple absorption band are tabulated, *viz.*, λ_{max} , the wave-length of maximum absorption, ϵ_{max} , the extinction coefficient at this wave-length, and δ , the width of the band, defined as the difference in wave-length of the two points on the curve for which $\epsilon = \frac{1}{2}\epsilon_{\text{max}}$. The b.p. and dipole moments, μ , of the solvents are also given. The latter are mean values taken from a recent table of dipole moments.¹⁵

¹⁴ Cf. Baskerville and Hamor, *Ind. Eng. Chem.*, 1912, 4, 571.

¹⁵ Sidgwick, *Trans. Farad. Soc.*, 1934, 30, Table of Dipole Moments.

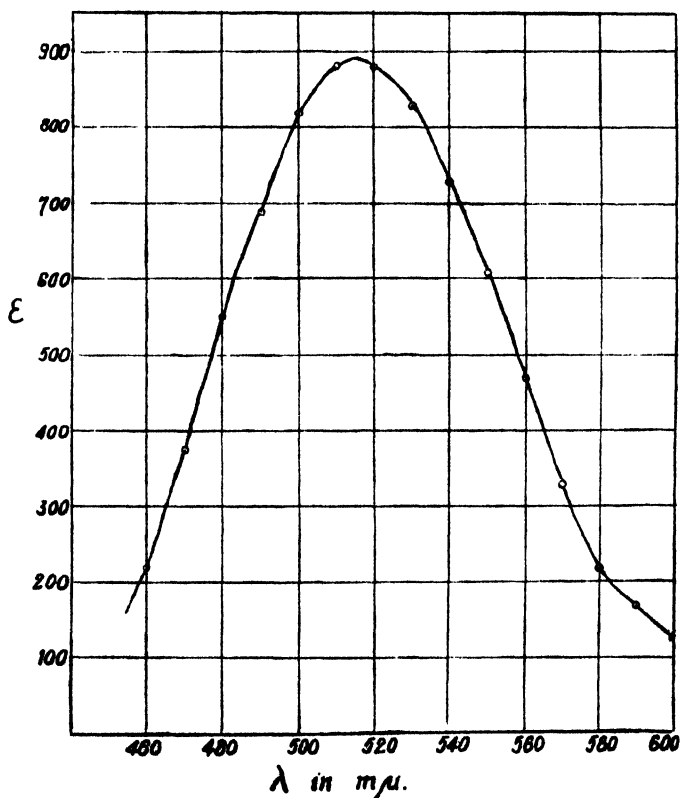
TABLE I.

Solvent.	B.P.	μ .	$\lambda_{\text{max.}}$ m μ .	$\epsilon_{\text{max.}}$	δ . m μ .
1. CCl_4	76.8	0	516	890	88
2. CHCl_3	61.2	1.1	511	880	90
3. $\text{CH}_2\text{Cl}_2 + \text{CCl}_4$	—	—	507	840	87
4. CH_2Cl_2	40.2	1.6	502	840	85
5. $\text{C}_6\text{H}_5\text{Cl}$	83.2	1.3-1.6	500	870	87
6. <i>n</i> - $\text{C}_6\text{H}_5\text{Cl}$	46.7	2.0	495	865	90
7. <i>n</i> - $\text{C}_6\text{H}_5\text{Cl}$	78.1	2.0	495	840	83
8. <i>trans</i> - $\text{C}_2\text{H}_4\text{Cl}_2$	49.0	0	518	680	81
9. <i>cis</i> - $\text{C}_2\text{H}_4\text{Cl}_2$	60.0	1.8	510	760	79

Discussion.

(a) Solutions of I_2 in CCl_4 .

It seems generally accepted that in CCl_4 , the molecules of which are symmetrical and have no resultant dipole moment, there is no solvation

FIG. 1.— I_2 in CCl_4 .

of the I_2 molecules. The inertness of this solvent is supported by the work of Chatelet¹⁸ who found Beer's Law valid for solutions of I_2 in

CCl_4 over a wide range of concentration. In the course of this work it was found that the absorption curve of a solution which had been kept in the dark for three months, was unchanged.

Some interaction due to van der Waals forces between I_2 and solvent molecules is to be expected even in the case of solutions in CCl_4 . It would be of interest to compare the values of λ_{max} and ϵ_{max} for the solution with those for I_2 vapour. The only extinction measurements available for the vapour are those of Vogt and Königsberger.¹⁶ From their data one can calculate, for the region of low pressures in which they found Beer's Law valid, a mean value of ϵ_{max} of 850 (for temperatures of 48-56°), in good agreement with the values for violet solutions (*cf.* Table I.). For I_2 pressures corresponding to a concentration of 0.001M, however, the values of ϵ_{max} are much lower. Vogt and Königsberger found λ_{max} for the vapour to be about 506 $\text{m}\mu$, but this result is questioned by Kuhn,¹⁷ who states that it should be about 400 Å, on the U.V. side of the convergence limit at 4995 Å, *i.e.*, at about 460 $\text{m}\mu$. This statement is based only on analogy with the corresponding values for Br_2 and Cl_2 . In the absence of reliable extinction coefficient data for I_2 vapour, therefore, it is not possible from absorption measurements to ascertain the existence or magnitude of any solvation effect for I_2 in a solvent like CCl_4 . In examining the influence of the dipole moment of the solvent, however, it is convenient to take CCl_4 as the reference solvent.

In Table II., the values of λ_{max} and ϵ_{max} for dilute solutions of I_2 in CCl_4 obtained by different

TABLE II.

Observer.	Solutions of I_2 in CCl_4 .	
	λ_{max} . $\text{m}\mu$.	ϵ_{max} .
1. Brode ¹⁸ . . .	517	913
2. Groh ¹ . . .	518	918
3. Getman ⁸ . . .	540	820
4. Gillam and Morton ⁸	520	985
5. Groh and Papp ¹⁹ .	518	922
6. Chatelet ¹⁸ . . .	517.5	864
7. Walker (<i>this paper</i>)	516	890

observers are compared. These give a concordant mean value of $518 \pm 2 \text{ m}\mu$ for λ_{max} , if one omits Getman's figure, which appears to be about 20 $\text{m}\mu$ too high. His values of λ_{max} for solutions in other solvents are also about 20 $\text{m}\mu$ higher than those of other workers. The mean value of ϵ_{max} for solutions in CCl_4 is about 900, and the agreement in this case is good considering the variety of methods employed and the rather large

experimental error: five of the values quoted do not differ by more than ± 4 per cent. from the mean.

(b) Solutions of I_2 in other Solvents.

Table I. shows that with increasing polarity of the solvent molecules λ_{max} is displaced to lower wave-lengths from a value of 516-518 $\text{m}\mu$ for the two non-polar solvents, indicating an increasing attraction of the solvent molecules for I_2 . A solution in a mixture of equal volumes of CCl_4 and CH_2Cl_2 has a value of λ_{max} intermediate between those of the solutions in the pure solvents. One should not, of course, expect

¹⁶ Vogt and Königsberger, *Z. Physik*, 1923, 13, 292.

¹⁷ Kuhn, *Z. Physik*, 1926, 39, 87.

¹⁸ Brode, *J. Amer. Chem. Soc.*, 1926, 48, 1877.

the amount of displacement to be related in a simple way to the dipole moment of the solvent (measured for the gaseous state, or in dilute solution), since other factors will obviously have to be taken into account, *e.g.*, the dipole moment and the polarisability of the individual links of the molecule, and stereo-chemical effects which may hinder the approach of I_2 and solvent molecules. Scheibe¹¹ has shown from absorption spectrum measurements of ketones and other substances, that the influence of the solvent on the absorption of radiation by a molecule in solution may be manifested in two ways, *viz.*, by a shift of the whole band to longer or shorter wave-lengths, with a corresponding change in λ_{\max} , and secondly, by a change in the height or intensity of the absorption band. A third type of change may occur when a definite chemical reaction takes place between the solvent and the dissolved molecules with the production of one or more new molecular species, in which case the character of the absorption curve may be entirely changed.

A shift of the absorption band to lower wave-lengths indicates an increased stability of the molecule or part of the molecule responsible for the particular band. It appears that in the case of I_2 solutions such a displacement occurs mainly as a result of two processes, *viz.*, (a) polarisation of the I_2 molecule by the electrical field of the polar solvent molecule, and (b) formation of addition compounds between the I_2 and the solvent. The amount of displacement is usually much larger in the second case than in the first, *e.g.*, in solvents of the alcohol series, all of which have dipole moments of about 2.0 D, λ_{\max} is at about 440-450 $m\mu$, whereas in "violet" solvents which have μ of the same order of magnitude λ_{\max} is displaced to about 500 $m\mu$ only.

It is clear, therefore, that the influence of the polar nature of the solvent can be made apparent only by a careful choice of solvents. This is also seen if one compares λ_{\max} for solutions of I_2 in a number of non-polar solvents, *e.g.*, CCl_4 , C_6H_{14} , CS_2 and C_6H_6 . For solutions in the first three solvents $\lambda_{\max} = 518 m\mu$,¹⁰ whereas in C_6H_6 , as has been mentioned, there is a displacement of the band towards the U.V.—values of λ_{\max} as low as 494.5 $m\mu$ have been recorded. The nature of the solvation effect in benzene solutions still seems uncertain.²⁰ Ornstein and Burgers²¹ have measured the absorption spectra of I_2 in benzene, toluene and xylene and obtained values of $\lambda_{\max} = 497$, 488 and 463 respectively, which shows that the solvation is greater in the two more polar solvents.

In the case of the solutions in the two unsaturated dichloroethylenes the intensity of the absorption band is also reduced compared with the intensity in the other violet solutions. This suggests some chemical reaction of I_2 molecules with the solvent, possibly addition of I_2 at the double bond. The difference in λ_{\max} for the two solutions affords a good example of the influence of the dipole moment of the solvent in displacing the absorption band.

In conclusion, it is of interest to summarise the various types of interaction which can take place between I_2 and solvent, and the corresponding changes in the absorption spectrum of the solutions.

(1) In violet solutions in inert, non-polar solvents (*e.g.*, C_6H_{14} , CCl_4) the interaction is probably due to van der Waals forces only. λ_{\max} is at about 516-518 $m\mu$ and the colour of these solutions is very similar to

¹⁰ Groh and Papp, *Z. physik. Chem.*, 1930, 149, 153.

²⁰ Cf. also Müller, *Physik. Z.*, 1933, 34, 703.

²¹ Ornstein and Burgers, *Akad. Amst. Verh.*, 1920, 29, 573.

that of the vapour, for which λ_{\max} is uncertain. Benzene, although it is a non-polar solvent, is exceptional.

(2) In polar solvents (*i.e.*, those having a resultant dipole moment) which do not have much chemical attraction for the I_2 molecules (*e.g.*, the halogeno-paraffins) there is an attractive force due to polarisation of the I_2 molecules by the electrical field of the solvent molecules. λ_{\max} may be displaced to 490-500 $m\mu$ and the solutions are violet-red in colour. The magnitude of the displacement (up to about 20 $m\mu$) is of the order to be expected from an attractive force of the van der Waals type.

(3) In solvents of the class described by Lachmann²² as "unsaturated" (*e.g.*, alcohols, ethers, nitriles, etc.), chemical valency forces result in the formation of molecular addition compounds between I_2 and solvent molecules. λ_{\max} is displaced to about 440 $m\mu$ and the solutions are red-brown in colour.

(4) With many of the solvents of class (3) further chemical reaction occurs in which I atoms replace H atoms in the solvent molecule, with the formation firstly of HI , and then, as a secondary reaction, of HI_2 . This is accompanied by a gradual disappearance of the brown colour and by the appearance in the absorption spectrum of the more intense bands at 350 and 290 $m\mu$ characteristic of HI_2 .

These remarks apply to dilute solutions of I_2 . In more concentrated solutions there may also be interaction of I_2 molecules with one another (*cf.* Groh and Papp¹⁹). In some cases, particularly in the brown solutions, colloidal complexes may be formed.²³

I should like to thank Dr. W. R. Angus, Dr. E. Teller and Dr. J. Weiss for helpful discussion.

Summary.

(1) Measurements have been made of the molecular extinction coefficient, ϵ , between 440 and 600 $m\mu$ for violet solutions of I_2 in the following solvents:

(1) CCl_4 , (2) $CHCl_3$, (3) CH_2Cl_2 , (4) $C_2H_4Cl_2$, (5) $n-C_2H_5Cl$, (6) $n-C_4H_9Cl$, (7) *cis*- and (8) *trans*- $C_2H_4Cl_2$.

(2) For solutions in the two non-polar solvents (1) and (8) λ_{\max} is at 516-518 $m\mu$. For solutions in the other solvents λ_{\max} is displaced towards the U.V., the displacement increasing roughly with the dipole moment of the solvent. The height and width of the absorption band in solutions 1-6 are approx. constant.

(3) The various types of interaction between I_2 and solvent are discussed with regard to their influence on the absorption spectrum of I_2 .

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²² Lachmann, *J. Amer. Chem. Soc.*, 1903, 25, 50.

²³ Chirnoaga and Chirnoaga, *Z. anorg. Chem.*, 1934, 218, 273.

THE SOLUBILITY OF HYDROGEN IN MOLTEN ALUMINIUM.

By L. L. BIRCUMSHAW, M.A., D.Sc.

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Precise determinations of the solubility of hydrogen in molten aluminium have been attempted by three different workers: Iwasé,¹ Czochralski² and Röntgen and Braun.³ The results obtained by these observers differ very considerably and in view of the importance of an exact knowledge of the solubility of hydrogen in aluminium and its alloys for the general question of the effect of gases on these metals it was considered desirable that further determinations should be made.

Experimental.

The method used was similar to that employed by Sieverts⁴ and by Röntgen and Braun and consists essentially in the use of a calibrated gas thermometer at constant pressure, the absorbed gas being measured on a calibrated gas burette. Great difficulty was experienced in the selection of a tube to contain the metal (placed in an alumina boat). It is well known that fused silica at the maximum temperature of the present work (1000° C.) is slightly permeable to hydrogen, sufficient to upset the results, so an apparatus was constructed, using a special porcelain tube as a container; this was found to be quite unsatisfactory, the tube absorbing small quantities of hydrogen continuously over considerable periods of time. It was then decided to surround the container with an atmosphere of hydrogen and after a number of trials the apparatus described below was constructed (Fig. 1).

The steel flange A is welded on to the end of a gas cylinder B (44.0 cms. long, 15.0 cms. diam.). The silica tube D fits through a central hole in the flange and the hollow water-cooled end plate C. The clear fused silica container tube E is waxed into position in the water-cooled collar F and the end of E is closed by a copper plate perforated by two circular holes. Short copper tubes are soldered on to these holes. Through I passes a silica tube fused into the hollow silica plug G which serves to take up the dead space of E, while J serves as an entrance to E. The collar F is soldered on to a wider copper collar K which fits up against the end plate C and into which fits the tube L. The metal is contained in an alumina boat M and the space between D and the walls of the gas cylinder is filled with asbestos wool. A small brass pin (2 mm. long) is soldered on to the inner surface of H and the silica plug is pulled forward until the face touches the end of the pin. The joint between H and the collar is then made gas-tight with wax. The joints between K and the end plate C and the joint between C and A are also made tight with wax. J is connected through a two-way tap to the gas burette, pumps and McLeod gauge, so that E can be either evacuated or filled with gas from the burette. Through I the plug can be either evacuated or filled with hydrogen and the space between the two tubes

¹ Iwasé, *Sci. Rep. Tohoku Univ. Ser. I.*, 1926, 15, 4.

² Czochralski, *Z. Metallk.*, 1922, 14, 277.

³ Röntgen and Braun, *Metallwirtschaft*, Aug. 19, 1932.

⁴ Sieverts, *Z. Metallk.*, 1929, 21, 37.

* Sieverts found no solubility of hydrogen in aluminium.

D and E can be similarly dealt with by means of the tube L. The body of the furnace can be filled with hydrogen through the tubes N and an opening (not shown) on the inner surface of A. The thermocouple is led through a small waxed hole (not shown in the diagram) and lies at X. The gas burette is contained in a large tank of water kept at $20^{\circ} \pm 0.05$. The burette can be read to 0.02 c.c.

The method employed was extremely simple. It consisted, at a particular temperature, in determining the volume of gas required to fill the

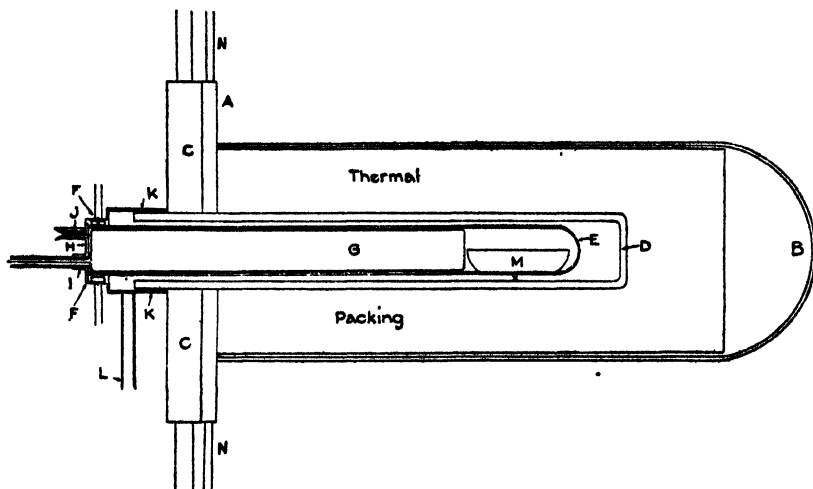


FIG. 1.

evacuated tube containing the boat followed by a determination of the volume required to fill the tube when the boat contained an accurately weighed quantity of metal. The difference between the latter volume and the former (corrected for the volume occupied by the metal at that temperature reduced to 20°) gives the amount of gas absorbed by the metal. The formula used for calculating the density of the metal at the required temperature is

$$\Delta = 2.378 - (0.000272)(t - 658^{\circ})$$

where Δ is the density at t° and 2.378 is the density at the freezing point.

TABLE I.

700°.		900°.	
Initial reading 16.50 c.c. at 3.10 p.m.,		20.98 at 2.50 p.m.	
16.29	3.17	20.70	2.55
16.28	3.25	20.63	3.5
16.27	3.35	20.56	3.20
16.22	3.50	20.55	3.35
16.22	4.0	20.54	3.50
16.20	4.12		
16.21	4.30		

The metal used was very pure metal supplied by Aluminium Foncé and was degassed by heating *in vacuo* for twelve hours before use. The hydrogen was generated electrolytically, freed from traces of oxygen by passage over

iron gauze, heated to 650° , and dried over silica gel. The boats were also degassed by heating *in vacuo* for twelve hours. It was found that in performing the calibrations when the tube was filled with gas by carefully

opening the tap of the burette and the mercury levelled a relatively rapid small rise took place followed by a slow, very small rise. This is shown by typical calibration experiments at 700° and 900° (Table I.).

The reading obtained after one hour, when the rate of rise was zero or nearly zero, was taken as the final value. This small drift from the initial

TABLE II.

Temp. °C.	Wt. of Al.	c.c. H ₂ abs. 20° C.	Pressure.	c.c. H ₂ (N.T.P.)/100 gms. Al.
700°	35.509 gms.	0.09	766 mm.	0.23
800°	36.738 "	0.31	776 "	0.79
	37.396 "	0.39	777 "	0.99
900°	36.642 "	0.77	768 "	1.98
	34.541 "	0.66	759 "	1.77
1000°	36.812 "	1.48	760 "	3.75
	37.784 "	1.60	765 "	3.98

reading after levelling may possibly be due to a slight alteration of temperature gradient along the furnace on the introduction of gas to the interior of E or more probably we may be measuring a small "activated" absorption of hydrogen by the alumina⁵ boat.

It was found that heating aluminium in a fairly good

vacuum (0.002 mm. mercury) undoubtedly led to the volatilisation of small quantities of the metal at temperatures as low as 800°. Thus an attempt to de-gas a sample of the metal practically destroyed one of the silica tubes (E) by attack from the aluminium vapour. All the metal used was therefore de-gassed in a subsidiary furnace. During a determination the spaces between the tubes D and E and the plug G were filled

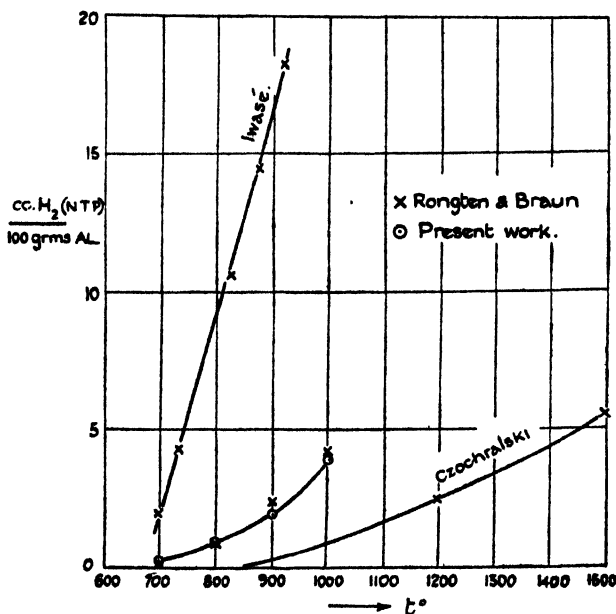


FIG. 2.

with hydrogen and in order to prevent any volatilisation of the metal the tube E was filled with argon. When the temperature of the furnace had become steady this gas was rapidly pumped off and hydrogen admitted from the burette.

⁵ H. S. Taylor, *Z. physik. Chem. Bodenstein. Festband.*, 1931, p. 475.

The results are shown in Table II. and graphically in Fig. 2, where for comparison the data obtained by Iwasé, Röntgen and Braun and Czochralski are also plotted. It will be seen that the present results agree

quite reasonably with those obtained by Röntgen and Braun.

Röntgen and Braun mention that in most of their experiments equilibrium was attained instantly. Curves are shown (in Fig. 3) of the burette readings (from an arbitrary zero) of the absorption of gas with time by the boat alone and the boat containing metal. The boat is in approximately the same condition, as regards containing traces of gas, in the two cases, so if all the gas dissolves before the first reading can be obtained (about one minute) the curve showing the measured absorption with time should be identical with the curve for that of the empty boat. This is seen to be

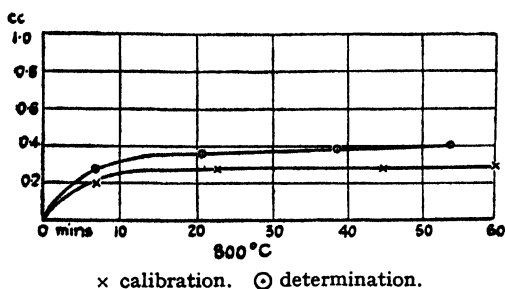
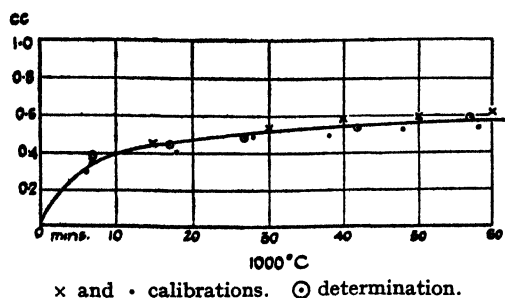


FIG. 3.

so at 1000° but at 800° it is interesting to note that final equilibrium does not appear to be reached until 15-20 minutes, during which time about

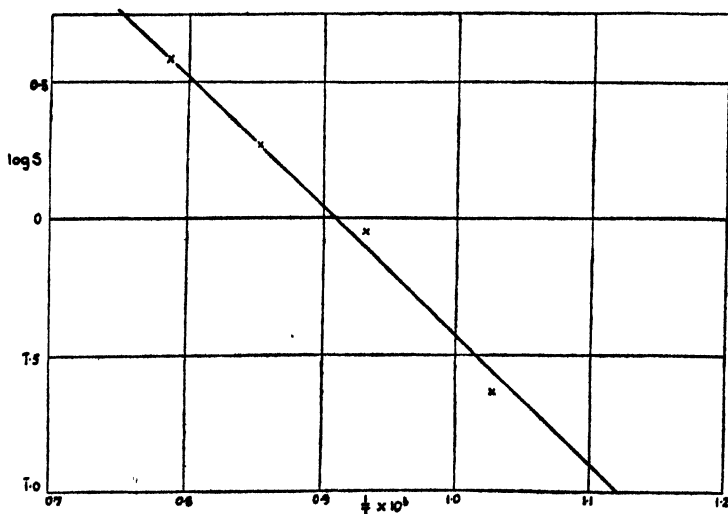


FIG. 4.

25.0 per cent. of the gas dissolves, the remaining gas having dissolved almost instantly.

Application of the van't Hoff isochore enables us to calculate the heat of solution.* We have

$$\frac{d(\log_e S)}{dT} = \frac{Q}{2RT^2}$$

which on integration gives

$$\log_e S = -\frac{Q}{2RT} + \text{const.}$$

$\log_e S$ plotted against $1/T$ gives a fairly good straight line (Fig. 4) from which Q has been evaluated and is 43,400 cal./gm. mol. This is the "saturated" heat of solution. It has been suggested that the ability of a metal to dissolve a gas depends on its ability to dissociate the gas.⁶ If this were true it might have been expected that Q might approximate to the heat of dissociation of hydrogen which is, however, in the region of 100,000 cal./gm. mol.

Summary.

The solubility of hydrogen in molten aluminium has been determined at 700°, 800°, 900° and 1000° C. and the volumes (N.T.P.) of gas dissolved are 0.23, 0.89, 1.87 and 3.86 c.c. per 100 gms. of metal respectively.

The "saturated" heat of solution has been calculated and has been found to be 43,400 cal./gm. mol. of gas dissolved.

The author would like to thank Dr. C. H. Desch, F.R.S., for his continued interest and valuable advice during the course of this investigation and Mr. J. Trotter for assistance in the experimental work. He would also like to thank the Metallurgy Research Board for permission to publish these results.

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* The assumption has been made that the gas dissolves as atoms which necessitates the "2" in the denominator of the above expression.

⁶ W. C. McC. Lewis, *J. Chem. Soc.*, 1920, 117, 623.

THE ACTION OF CHARCOAL ON AQUEOUS SOLUTIONS OF SILVER NITRATE.

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It has been known for a considerable time that certain metallic salts in aqueous solution undergo reduction by contact with charcoal.¹ Until recently the charcoals investigated were prepared from complex materials containing hydrogen.² Hence it was natural to suppose that the reducing properties of the charcoal might be due simply to the presence of

¹ H. Freundlich, *Kapillarchemie*, 1930, 1, 324.

² See, for example, J. W. Mellor, *Inorganic and Theoretical Chemistry* (London), 1923, 3, 473; 1924, 3, 832.

hydrocarbons, or hydrogen, produced by the decomposition of the original substance. Recently, however, Heymann, Salomon, and Kieffer³ have observed reduction in the case of charcoal prepared by passing carbon tetrachloride vapour over heated mercury. Since this method of preparation excludes the formation of hydrocarbons, or hydrogen, it must be concluded that the carbon itself is involved in the reducing process.

Further investigation is required in order to ascertain the precise manner in which the charcoal acts. In particular it is necessary to know the actual amount of reduction under any given set of conditions. The fact that the determination of the amount of reduction is complicated by the adsorption of the substance undergoing reduction, and of the products of reduction, probably accounts for the lack of essential data. It will be shown that in the case of silver salts, the amount of reduction may be accurately estimated by a simple method.

Hitherto the action of charcoal on silver salts in aqueous solution has not been studied in detail. Morawitz⁴ observed that when a solution of silver sulphate, or acetate, was shaken with charcoal, the silver content of the solution decreased rapidly for a short time, and then much more slowly over a long period. It was also found that acid appeared in the solution, and that the tendency of silver to disappear from the solution was more pronounced in the case of the acetate, than in the case of the sulphate. Bartell and Miller⁵ have examined the action of ash-free charcoal, prepared from sugar, on solutions of silver nitrate, sulphate, and acetate. They found that sufficiently dilute solutions remained neutral, though deprived of the whole of their silver, whereas more concentrated solutions became acid. Ruff, Ebert, and Luft⁶ investigated the X-ray spectra obtained with various charcoals after contact with either a neutral solution of silver nitrate or one to which nitric acid had been added. Interference lines, characteristic of metallic silver, were obtained, provided the concentration of acid did not exceed a certain value. Warlet,⁷ who also worked with sugar charcoal, has shown that a portion of the salt, in a solution of silver nitrate, is simply adsorbed by the charcoal, and can be recovered by treating the latter with water.

In view of the foregoing, attention in the present work was directed to the influence of (1) concentration of silver nitrate, (2) time of contact between charcoal and solution, (3) acidity of solution, and (4) treatment of charcoal, on the amounts of adsorbed silver, reduced silver, and liberated acid.

Preparation of Charcoals.

Small portions of A.R. saccharose (Hopkin and Williams, Ltd.) were charred, powdered, and heated with a full méker flame for forty minutes in a silica basin covered with a loosely fitting lid, the charcoal being stirred every five minutes. The charcoal was then ground in a carefully cleaned agate mortar and stored in a tightly stoppered bottle. Two grams of this charcoal (C₁) on complete combustion gave 0.0004 gram ash, free from iron. Charcoal C₁ served as the starting material in the preparation of all the charcoals investigated. A summary of the treatment in each case is given in Table I.

³ E. Heymann, K. Salomon, and R. Kieffer, *Z. anorg. Chem.*, 1930, 187, 97.

⁴ H. Morawitz, *Kolloid-Beih.*, 1909-1910, 1, 301.

⁵ F. E. Bartell and E. J. Miller, *J. Amer. Chem. Soc.*, 1923, 45, 1106.

⁶ O. Ruff, F. Ebert, and F. Luft, *Z. anorg. Chem.*, 1928, 170, 49.

⁷ M. Warlet, *Bull. Soc. chim. Belg.*, 1933, 42, 127.

TABLE I.—PREPARATION OF CHARCOALS.

Charcoal.	Treatment.
C ₁	C ₁ heated in open silica basin at 740-830° for 30 mins.
C ₂	C ₂ heated in stream moist air at 450-455° for 11 hrs.
C ₃	C ₃ heated in stream dry air at 450-455° for 11 hrs.
C ₄	C ₄ treated with dry chlorine for 2 hrs., then hydrogen for 2 days, and finally dry oxygen for 3 hrs. Temperature throughout 460-465°.
C ₅	C ₅ heated in stream dry oxygen at 450-470° for 3 hrs.
C ₆	Same as C ₅ .
C ₇	Same as C ₅ .
C ₈	C ₈ heated in stream dry air at 980° for 4.5 hrs.
C ₉	C ₉ treated with dry carbon dioxide at 1010° for 5 hrs.
C ₁₀	C ₁₀ degassed at 1125° for 1 hr., under a pressure of 1 mm. Hg.
C ₁₁	C ₁₁ treated with moist air at 1125° for 4 hrs.
C ₁₂	C ₁₂ heated in carbon dioxide at 1250° for 35 mins.
C ₁₃	C ₁₃ kept at room temperature for 1 month in an evacuated vessel containing phosphorus pentoxide.
C ₁₄	C ₁₄ treated with stream very dry nitrogen at room temperature for 1 month.
C ₁₅	

Experimental Procedure.

In the standard procedure finally adopted, 0.2 gram of charcoal was shaken at room temperature with 10 c.c. of silver nitrate solution in a sealed glass tube, fixed radially on a slowly revolving wheel. Immediately on completion of the period of shaking, normally twenty-four hours, the solution was decanted through a fine filter paper, and the silver content determined by titration with potassium thiocyanate. Over the range of concentration of silver nitrate involved, acid invariably appeared in the solution on shaking with the charcoal. The amount of such acid (liberated acid) was determined by titration with sodium hydroxide, using phenol red as indicator. It proved possible to estimate both acid and silver in the same sample of solution as follows. The acid was first titrated, the solution being boiled to ensure a sharp endpoint, the colour of the indicator then destroyed by heating with 2 c.c. of concentrated nitric acid, and the silver estimated as usual. To complete the experiment, the charcoal was transferred to the filter paper, washed with water to remove the bulk of the remaining silver nitrate, and immersed in 0.3 *M* potassium chloride for thirty minutes. After washing until free from chloride, the charcoal was boiled for one hour with approximately 8 *M* nitric acid, and determination made of the amount of silver extracted by the acid.

The quantity of silver, say x micro-equivalents, extracted from the charcoal by the acid was always less than that, say y micro-equivalents, which had originally disappeared from the solution. If the treatment with potassium chloride was omitted, and the charcoal repeatedly washed with water, silver reappeared in solution, in amount equal to the difference $y - x$. Extraction with nitric acid again yielded x micro-equivalents, so that the whole of the silver was recovered. It was further observed that particles of pure silver, often of considerable size, were produced by the action of the charcoal. In two experiments a quantity of the metal was separated from the charcoal by floating off the latter, and found to amount to about 50 per cent. of the value of x for the given conditions. More efficient separation would undoubtedly have shown that the total amount of silver in the form of metallic particles was actually x , or almost so. It is evident that part (x) of the silver nitrate was decomposed by the charcoal, the silver ions being reduced to atoms of the metal, which did not remain on the surface of the charcoal, but formed independent aggregates. The remainder of the silver ($y - x$) which disappeared from

the solution on shaking with charcoal, was not reduced, but reversibly adsorbed, and could be recovered by extraction with water, or precipitated by treatment with potassium chloride.

In the routine procedure described above, the adsorbed silver was precipitated as chloride, the reduced silver extracted with nitric acid and estimated directly, and the adsorbed silver found by difference. This procedure was much more rapid and convenient than extracting the adsorbed silver with water and estimating its amount directly. The reliability of the method was tested in the following manner. About 0.2 gram of charcoal (C_3) was shaken for twenty-four hours with 10 c.c. of 0.2497 *M* silver nitrate. Ten c.c. of 0.2593 *M* potassium chloride were now added, the charcoal and silver chloride filtered off, and the concentration of potassium chloride in the filtrate determined by Mohr's method (the liberated acid having been neutralised with sodium hydroxide). Assuming that the decrease in chloride was wholly due to precipitation of silver, the amounts of unprecipitated silver in two independent experiments were found to be 743 and 757 micro-equivalents per gram charcoal. The charcoal was washed with water and extracted with nitric acid in the usual way, and the extracted silver found to be 721 and 748 micro-equivalents respectively. In these experiments the charcoal was left in contact with the potassium chloride for thirty minutes. Experiments were also performed, of exactly the same nature as the foregoing, except that eighteen hours were allowed to elapse before the charcoal and potassium chloride were separated. In two such experiments the unprecipitated silver amounted to 760 and 765 micro-equivalents, and the silver extracted with nitric acid to 737 and 753 micro-equivalents respectively. The values for reduced silver obtained in three experiments with the same charcoal and concentration of silver nitrate, but employing the normal method of analysis, proved to be 741, 747, and 737 micro-equivalents.

These results showed that the standard procedure ensured—(1) complete precipitation of the adsorbed silver, (2) complete elimination of the excess of potassium chloride; otherwise a portion of the silver extracted with nitric acid would have been precipitated as chloride, and a low result obtained for the reduced silver, (3) complete extraction of the reduced silver. They also indicated the absence of interaction between the metallic silver and the potassium chloride, which agreed with the observation that pure silver wire was unaffected by immersion in 0.3 *M* potassium chloride for eighteen hours. It would therefore appear that the analytical procedure was satisfactory.

Influence of Period of Contact.

Table II. illustrates the manner in which the results depended upon the length of time the charcoal was kept in contact with the silver nitrate solution. It will be seen that the amount of silver nitrate adsorbed was more or less independent of the period of shaking, being substantially the same after one month as after ten minutes. The amount of reduction, however, varied markedly with time, increasing, between twenty-four hours and one month, to a maximum value of about 1260 micro-equivalents per gram charcoal at the two lower concentrations, but decreasing, during the same period of time, when the concentration was 0.995 *M*. It appeared that in the last case interaction occurred between the liberated acid and the metallic silver. The quantity of coarse silver visibly decreased when the period of shaking was extended from twenty-four hours to one month. Moreover, during this interval the liberated acid decreased by an amount equivalent to the decrease in reduced silver, the actual changes being 311 and 276 micro-equivalents (mean values) respectively. It is difficult to account for the re-solution of the silver at high concentrations of silver nitrate, since the concentration of liberated acid was no greater than at the lower concentrations of the silver salt, and in any case was less than

TABLE II.—INFLUENCE OF VARIATION IN PERIOD OF CONTACT (CHARCOAL C₉).

Initial Concentration Silver Nitrate.	Period of Shaking.	Adsorbed Silver.	Reduced Silver.	Liberated Acid.	Adsorbed Silver + Adsorbed Acid.
0.0992 <i>M</i>	24 hrs.	608	687	509	786
		597	727	491	833
	24 days	472	1266	1025	713
	1 month	516	1217	949	784
		713	1082	972	823
0.4803 <i>M</i>	10 mins.	1267	566	371	1460
	4 hrs.	1298	712	513	1487
	24 hrs.	1308	1027	647	1688
		1135	1049	710	1474
		—	1012	660	—
	5 days	1372	1115	927	1560
	1 month	1370	1391	1053	1729
		1368	1261	—	—
0.9550 <i>M</i>	24 hrs.	—	1041	652	—
		—	1040	660	—
	1 month	—	811	293	—
		—	717	397	—
		—	—	—	—

0.01 *M*.^a A possible explanation is that the silver nitrate was contaminated with some polyvalent metal which exerted a catalytic effect, but was present in such minute amounts that its action was appreciable only at high concentrations of silver nitrate.^a

Reduction did not continue indefinitely, but ceased within a month, at least for the concentration (initial) range 0.099–0.48 *M*. Ruff, Ebert, and Luft^b consider that reduction comes to an end when the ratio of the concentrations of silver and hydrogen ions attains a certain value. The present observations (Table II.) do not support this view, since the total reduction was found to be the same for 0.0992 *M* and 0.48 *M* silver nitrate, although the values of the ratio in question were 0.33 and 2.15 respectively.

The data in Table II. also show that the quantity of acid which appeared in the solution was less than the amount of silver reduced. Hence a certain amount of the acid produced by the reduction remained adsorbed on the charcoal. In the last column of the table is given the sum of the amounts of adsorbed silver and adsorbed acid, and it will be seen that, for a given concentration of silver nitrate, this quantity is more nearly constant than the adsorbed silver alone.

Influence of Concentration of Silver Nitrate.

The data obtained with almost all the charcoals gave curves of the type shown in the accompanying figure, when the period of contact between charcoal and solution was twenty-four hours. While the amount of silver adsorbed ($y-x$) increased continuously with increase in concentration of silver nitrate, the quantity of silver reduced, and of acid liberated, became practically constant for concentrations (final) greater than about 0.45 *M*. In a few cases measurements were made with 2.0 *M* silver nitrate, and the reduction found to be somewhat lower than with 1.0 *M*, owing probably to the effect described in the preceding section.

^a L. Marchlewsky, *Ber.*, 1891, 24, 2269.

^b H. Freundlich and K. Soellner, *Kolloid. Z.*, 1928, 44, 309.

Assuming that reduction is preceded by the adsorption of silver ions on the reducing atoms of the charcoal surface, it follows that the rate of reduction will depend upon the degree to which such adsorption takes place. According to this, the shape of the reduction curve indicates that when the concentration of silver nitrate is $0.45\text{ }M$ or more, the reducing portion of the charcoal surface is saturated with silver ions immediately contact is made between the charcoal and the solution.

From the data in Table II. it will be seen that for the most part the reduction proceeded quite slowly. Even in the case of $0.48\text{ }M$ silver nitrate (final concentration about $0.43\text{ }M$) the reduction was not complete in twenty-four hours, although the reducing surface was saturated with silver ions from the beginning. It would appear that there is a time lag

in the tendency to reduction, which varies from point to point of the charcoal surface.

When the final concentration of silver nitrate was less than $0.45\text{ }M$, the reduction exceeded the adsorption of silver (see Table II. and Fig.). At low concentrations only part of the reducing surface was covered with silver ions, but since the adsorption is reversible, ions must be continuously vacating one part of the surface and occupying another. Hence eventually every reducing point will have been associated with a silver ion, so that the total reduction will be the same as at high concentrations of silver nitrate.

At concentrations of silver nitrate greater than $0.45\text{ }M$ the adsorption exceeded the reduction. It is possible that at high concentrations the adsorbed layer of silver nitrate is more than one molecule thick, since on plotting the reciprocal of the adsorbed

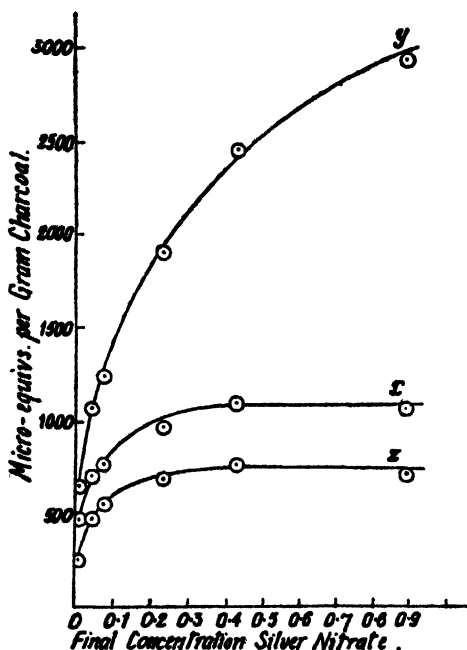


FIG. 1.—Charcoal C_7 . Curve y —total amount of silver removed from solution. Curve x —amount of silver reduced. Curve z —amount of acid liberated.

silver against that of the final concentration of silver nitrate, a straight line is not obtained, but a curve which is concave towards the $1/\text{concentration}$ axis.^{10, 11}

Influence of Acidity.

In Table III. are given the results obtained by shaking 0.2 gram charcoal C_8 (two months old) for twenty-four hours with 10 c.c. of solution containing both silver nitrate and nitric acid. The values for the amount of reduction show a rather surprising lack of consistency, but it is clear that the reduction decreased as the acidity was increased.

Heymann¹² assumes that reduction is preceded by hydrolytic decom-

¹⁰ I. Langmuir, *J. Amer. Chem. Soc.*, 1918, 40, 1360.

¹¹ C. Ockrent, *J. Chem. Soc.*, 1932, 1864.

¹² E. Heymann, *Z. anorg. Chem.*, 1932, 207, 251.

position of the silver salt at the surface of the charcoal. The silver hydroxide is immediately reduced, and a portion of the hydrolysis acid is set free in the solution. According to this view the inhibition of reduction by the addition of acid is due to the suppression of hydrolysis. The data in Table III., however, indicate a different interpretation, since there appears to be a definite relationship between the reduction and the adsorption of acid. Not only does the amount of adsorbed acid increase as the amount of reduced silver decreases, but the sum of these quantities remains roughly constant. This suggests that the action of the acid is to cover the reducing portions of the charcoal surface, so that they become inaccessible to the silver ions.

TABLE III.—INFLUENCE OF ACIDITY (CHARCOAL C₃).

Initial Concentration AgNO ₃ .	Initial Concentration HNO ₃ .	Reduced Silver.	Adsorbed Acid.	Reduced Silver + Adsorbed Acid.
0.1249 <i>M</i>	0.0486 <i>M</i>	568	282	850
	0.1157	498	372	870
	0.4629	199	599	798
		34	823	857
0.2493	—	737	135	872
	0.0486	624	242	866
	0.0926	606	305	911
		599	313	912
	0.2314	181	563	744
		129	576	705
0.5000	—	838	152	990
	0.0486	718	273	991
	0.0926	600	235	835
	0.2314	37	737	774
		158	576	734

Ageing of the Charcoal.

In a number of cases the behaviour of the charcoal was re-examined after it had been kept for some time. The charcoals included in Table IV.

TABLE IV.—INFLUENCE OF AGE OF CHARCOAL.

Charcoal.	Age.	Initial Concentration AgNO ₃ .	Reduced Silver (<i>x</i>).	Adsorbed Silver (<i>y</i> - <i>x</i>).	Adsorbed Acid (<i>z</i> - <i>x</i>).	Adsorbed Silver + Adsorbed Acid (<i>y</i> - <i>z</i>).
C ₃	Fresh, 2 months	0.2497 <i>M</i>	1041	719	364	1083
		0.2497 <i>M</i>	742	911	135	1046
C ₄	Fresh, 2 months	0.2497 <i>M</i>	786	790	188	978
		0.2497 <i>M</i>	662	850	121	971
C ₇	2 weeks 8 months	0.9550	1075	1877	353	2230
		1.0000	762	1897	218	2115
C ₈	2 weeks 8 months	0.9550	1009	2406	153	2559
		1.0000	733	2307	91	2398
C ₉	4 months 12 months	0.0992	707	603	207	810
		0.0992	510	580	157	737
C ₁₄	Fresh, 3 months	0.2497	1088	793	366	1159
		0.2497	784	893	225	1118
C ₁₅	Fresh, 3 months	0.2497	1017	843	307	1150
		0.2497	826	957	207	1164

were stored (in stoppered tubes) in the presence of air, and it will be seen that under these conditions the reducing capacity diminished with age. While the adsorption of acid generally also decreased, that of the silver nitrate increased to about the same extent, so that the total adsorption (acid + silver nitrate) remained practically unchanged (Table IV., last column).

Charcoal C_{14} was a sample of C_2 which had been kept, at room temperature, for one month in a vessel containing phosphorus pentoxide, and evacuated to a pressure of 6 mm. Hg. As shown in Table IV., the reduction produced by this charcoal when fresh, *i.e.*, immediately after removal from the evacuated vessel, was 1088 micro-equivalents in the case of 0.2497 M silver nitrate. A sample of C_2 stored for one month in the usual manner, gave reduction amounting to 989 micro-equivalents. The corresponding figures for 1.0 M silver nitrate were 1165 and 1101 micro-equivalents respectively. It therefore appears likely that the loss in reductive capacity experienced under ordinary conditions was due to the oxidation of surface atoms of the charcoal by atmospheric oxygen.¹³

Influence of Treatment of Charcoal.

Table V. contains data obtained with fresh charcoals in twenty-four hours at a final concentration of silver nitrate of 0.45 M .

TABLE V.—FINAL CONCENTRATION SILVER NITRATE = 0.45 M .

Charcoal.	Reduced Silver.	Adsorbed Silver.	Adsorbed Acid.	Reduced Ag Adsorbed Ag	Reduced Ag
					Ads. Ag + Ads. Acid.
C_3	1090	1160	370	0.94	0.71
C_4	920	1170	210	0.79	0.67
C_5	689	1051	2	0.66	0.65
C_6	810	976	204	0.83	0.69
C_7	1105	1371	336	0.81	0.65
C_{10}	675	526	425	1.28	0.71
C_{11}	600	700	240	0.86	0.64
C_{13}	300	260	210	1.15	0.64
C_{14}	1129	1326	361	0.85	0.67
C_{15}	1112	1294	339	0.86	0.68

hours (see Table II.), the total amount of silver reduced would be practically equal to the amount of silver adsorbed. This suggests that as the silver ions initially adsorbed are reduced and the metallic silver leaves the surface, the vacant spaces are immediately occupied by a fresh supply of silver ions, which, however, do not undergo reduction. For charcoal C_2 the ratio of reduced to adsorbed silver appeared to be only 0.66. In the preparation of this charcoal a sample of C_1 was first treated with chlorine at 460° in order to decompose hydrocarbons. Subsequent prolonged treatment with hydrogen to remove excess chlorine was not completely successful and traces of hydrochloric acid were retained by the charcoal. On shaking with silver nitrate, silver chloride was formed together with an equivalent quantity of nitric acid, which was adsorbed by the charcoal. Hence a fictitiously high value for the adsorption of silver was obtained, and practically complete liberation of the acid formed by reduction took place.

Table VI. gives the data for fresh charcoals when the final salt concentration was 0.75 M . Both tables show that while the ratio of reduced to adsorbed silver may vary considerably from charcoal to charcoal, the ratio of reduced silver to the sum of adsorbed silver and adsorbed acid is

¹³ H. H. Lowry and G. A. Hulett, *J. Amer. Chem. Soc.*, 1920, 42, 1408.

reasonably constant. It would therefore seem that in the case of charcoals C_{10} and C_{12} , the adsorption of acid was abnormally high, so that the ratio of reduced to adsorbed silver was also high.

The constancy of the ratio of reduced silver to the sum of adsorbed silver and adsorbed acid indicates that the variety of treatments to which the charcoal was subjected did not affect the progress of the reduction as such, but that change in the amount of reduction was simply due to change in the specific adsorbing area of the charcoal.

TABLE VI.—FINAL CONCENTRATION SILVER NITRATE=0.74 M.

Charcoal.	Reduced Silver.	Adsorbed Silver.	Adsorbed Acid.	Reduced Ag Adsorbed Ag	Reduced Ag Ads. Ag + Ads. Acid
C_3	1090	1665	380	0.66	0.53
C_4	920	1634	216	0.56	0.50
C_5	680	1380	0	0.49	0.49
C_6	840	1270	190	0.66	0.58
C_7	1090	1750	340	0.62	0.52
C_{11}	600	978	239	0.61	0.50
C_{12}	156	164	130	0.95	0.54
C_{13}	300	380	220	0.79	0.50
C_{14}	1140	1660	380	0.69	0.56
C_{15}	1080	1570	340	0.69	0.57

At high temperatures this would tend to decrease owing to graphitisation,¹⁶ which would account for the low reduction values in the case of charcoals C_{10} , C_{11} , C_{13} , and C_{15} . The low value for C_6 may be attributed to insufficient activation, and that for C_4 to the adsorption of hydrochloric acid on the reducing surface.

At the commencement of the investigation it was thought that chemi-adsorbed water might be of importance for the reduction, but the normal behaviour of the charcoal after treatment at high temperatures does not support this view.¹⁵ It was also thought that the reduction might be connected with the production of oxalic acid, observed by King,¹⁸ but it was found impossible to detect the presence of this acid, even under the prescribed conditions. Finally it should be pointed out that while charcoal C_3 gave the maximum adsorption of sodium hydroxide, in agreement with the work of Kolthoff¹⁷ and others, its reducing properties were unexceptional.

Summary.

1. Two processes can be distinguished in the action of charcoal on aqueous solutions of silver nitrate, *viz.*, (1) rapid adsorption of silver nitrate, and (2) much slower reduction of adsorbed silver ions to metallic silver.

2. The reduced silver does not remain on the charcoal surface but aggregates to form separate particles.

3. It would appear that only an amount of silver ion corresponding to a monomolecular layer of adsorbed silver nitrate undergoes reduction.

4. The carbon atoms which are oxidised through the reduction of the silver, retain their capacity of adsorbing silver nitrate.

5. At high concentrations of silver nitrate, the adsorbed layer of salt appears to be more than one molecule in thickness.

6. The suppression of reduction by the addition of acid appears to be due to selective adsorption of the acid on the reducing surface, so that this becomes inaccessible to silver ions.

¹⁴ R. M. Barrer and E. K. Rideal, *Proc. Royal Soc.*, 1935, **149A**, 231.

¹⁵ C. Ockrent, *J. Chem. Soc.*, 1934, 291.

¹⁶ A. King, *J. Chem. Soc.*, 1933, 842, and 1934, 22.

¹⁷ I. M. Kolthoff, *J. Amer. Chem. Soc.*, 1932, **54**, 4473.

7. On exposure to the atmosphere at room temperature the reducing capacity of the charcoal decreases, owing probably to oxidation of the active carbon atoms by atmospheric oxygen.

8. Variation of the amount of reduction with (1) degree of activation, and (2) temperature of treatment of the charcoal, appears to be due simply to variation in the specific adsorption surface of the charcoal.

9. The sum of the amounts of adsorbed silver and of adsorbed acid is independent of (1) time of contact between charcoal and solution, (2) degree of ageing of charcoal.

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THE RELATION BETWEEN DENSITY OF BLACKENING AND X-RAY INTENSITY FOR CHARACTERISTIC COPPER RADIATION AND AGFA-LAUE FILM.

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Although there are many methods by which the estimation of X-ray intensity can be carried out photographically without exact knowledge of the relation between intensity and density of blackening (*I.D.*) such knowledge is generally of the greatest use. Many investigations have been made to find out how far this relation is linear, but as a rule the times of exposure have been so short that the results could not be applied to the longer exposures which are more usual in practical work without assuming (on perhaps rather insufficient ground) that the Schwarzschild constant was unity. Only in certain cases has any attempt been made to examine characteristic wavelengths of radiation without the possible complications caused by the background.

The use of crystals to secure homogeneous radiation is becoming more common. For this and other reasons it was of great interest to examine the *I.D.* relation for a standard type of film and for a characteristic radiation ($\text{Cu}\alpha$) made as monochromatic as possible.

A Brief Survey of the Literature.

The literature of the subject is extensive. Only the more recent work, beginning with that of Bouwers, need be noticed. There are three interesting points with which it deals, (a) The form of the *I.D.* curve and the range in which it may be taken to be a straight line, (b) The possible—although unlikely—existence of a threshold value, and (c) The question whether the Schwarzschild constant is unity. The earlier references are given by Bouwers.^{1, 1a} This worker used the whole radiation given by

¹ Bouwers, *Z. Physik*, 1923, 14, 374.

^{1a} *Over het meten der Intensiteit van Röntgenstralen*, Thesis, Utrecht, 1924.

the target, but when characteristic lines were present (Pt. Mo. and Cu) appropriate filters were employed to remove the β component. The radiation was therefore always very far from being homogeneous. He found that the relation between density and time of exposure to a constant intensity was never strictly linear, but could be expressed by an equation already applied by Busé² to visible light which, since the Schwarzschild constant was proved to be very nearly unity, may be written

$$Z = C \log \left(\frac{It}{a} + 1 \right),$$

C and a being constants for given experimental conditions. C is independent of wavelength but varies from one kind of film to another. Since Sheppard and Mees³ found that the density increased with the time of development proportionally to the factor $(1 - e^{-bt})$, C also depends on the time of development.

Jönssen⁴ stated that the curve was convex to the axis of intensity, even near the origin, but Busse⁵ made a few measurements with monochromatised molybdenum and tungsten radiation, finding a linear relation up to $D = 0.8$ and concluded that Jönssen's results must be due to peculiar conditions of development. It is frequently stated that the developer must contain little or no bromide if a linear relation is to hold. Martin and Lang⁶ found strict proportionality to $D = 0.8$ for Agfa film and copper radiation. Cameron⁷ obtained a similar result. Other published results might be quoted but no general conclusion can be drawn.

Although it is improbable that there should be a threshold value for the action of X-rays in blackening the photographic film, the examination of the initial part of the scattering curve had not been properly carried out until recently. In a recent paper⁸ Brentano, Baxter and Cotton have described a photometer the action of which it to measure the scattered and not the directly transmitted light. With this instrument they have been able to extend the determination of density downwards into a region in which this quantity is too small for precise measurement in any other way. A linear relation was found to hold and no threshold could be detected.

It is interesting to note that when a large amount of potassium bromide was present in the developer they found an irregular rise for the lowest densities, so that the curve near to the origin was convex to the axis of density, as if there were an indefinite threshold. In the absence of bromide, or when only a little was used, no such effect appeared.

Experimental.

Principle of the Methods.—The beam issuing from the window of the tube falls on a calcite crystal set at the proper angle, and from this the characteristic radiation is reflected in a sheet which strikes the film and forms a vertical line. By various photometric devices this line can be divided into sections, one above the other, representing different amounts of illumination. By a lateral movement of the film holder the same line

² Busé, *Physica*, March, 1922, No. 3.

³ Sheppard and Mees, *Z. wiss. Phot.*, 1905, 3, 354.

⁴ Jönssen, *vide* ¹.

⁵ Busse, *Z. Physik*, 1925, 34, 11.

⁶ Martin and Lang, *Proc. Roy. Soc.*, 1932, 137, 199.

⁷ Cameron, *Physics*, 1932, 3, 58.

⁸ Brentano, Baxter and Cotton, *Phil. Mag.*, 1934, vii, 17,370.

is also recorded on each film without any photometric reduction of the intensity. The density of each section of the reduced line (D_r) is then found and also that of the unreduced line (D_u) at the same height. One section of the unreduced line (D'_u) is arbitrarily selected and each of the quantities D_r is then divided by the corresponding ratio of D_u/D'_u . In this way each value of D_r is altered to the value that it should have if the whole unreduced line were of density D'_u . It is assumed that in the small range of D_u , and in that in which D_r is changed by calculation, I and D are strictly proportional.

Two methods were used to graduate the radiation falling on the film, one employing a rotating sector and giving different relative times for the same intensity, the other making use of a stepped wedge of metal foil and giving different relative intensities for the same time. The two sets of results enable one to say whether the Schwarzschild constant is unity or has some other value; the simultaneous application of both methods to the same X-ray beam might be used to determine this value.

Apparatus and General Method.—X-rays were generated in a special gas-tube, the voltage of which was automatically held constant within 5 per cent. The calcite crystals were ground on the cleavage face by rubbing lightly with fine emery and water on a glass plate. The first crystal was fastened with wax to a rotatable holder in a lead housing fixed to the tube, and the beam passed through a hole in this housing and then on to the second crystal which was fixed to the table of the spectrometer. This instrument with its photometric apparatus could be rotated about a centre coinciding with the vertical axis of rotation of the first crystal so that the difficult adjustment of the two crystals was facilitated. The movable arm of the spectrometer was made parallel with the ray after its second reflection and on it was placed the film holder at about 15 cm. from the second crystal. Immediately in front of the holder was the sector wheel or the wedge, and in front of that a lead screen with a slit 4 mm. wide. Other screens were placed wherever any stray radiation could be intercepted. The film holder was about 5 cm. square and encased in lead with the exception of the front. The removable cover was of aluminium foil, and to prevent fogging through pinholes, two layers of foil were used each 0.01 mm. thick. The holder could be moved laterally to allow of five exposures on the same film.

The setting of the crystals and film holder had frequently to be repeated because the first crystal was rapidly roughened by the concentrated radiation. It was not difficult by working in almost complete darkness, to detect the second reflected ray on platinocyanide paper.

Even with this arrangement the vertical line formed on the film was far from homogeneous. As either crystal was turned through a small angle the maximum intensity flickered up or down the line. The effect is due partly to the difficulty of making two crystal faces exactly parallel but mainly to the imperfection of the calcite itself. To avoid it the second crystal was rocked through an arc of $20'$ by a small cam which was revolved to give about five throws back and forward each second. Other means which were effective in making the line more even and also broad enough for photometry were the insertion of a target with a face at an angle of 30° to the beam instead of the usual 10° or 12° and the enlargement of the focal spot by increasing the distance between target and cathode.

The Rotating Sector Method.—The sector wheels were cut from thin lead sheet, the edges being bevelled to cut off the beam sharply, and were of the usual form. There were eight steps each 2.5 mm. in height giving a total length of reduced line of 16 mm. in addition to 2.5 mm. of unreduced line produced by the beam at the outer extremity of the wheel. The relative angular values of the openings are given in Fig. 1. They were selected so that the results could be plotted in two separate ranges and were measured on the goniometer.

The wheel was rotated at not more than three revolutions a minute.

so that the time of opening of the smallest slot was not less than 0.4 second. In this time the crystal passed through the reflection position four times and the X-ray tube, working as usual with 50 cycle alternating current and half-wave rectification gave twenty discharges, of which about one-third occurred when a reflection was actually taking place. Given fair constancy of the voltage, which was maintained by the automatic regulator, these rates were such that variations of the incident intensity could not be caused by the intermittency of any of the operations.

When it was necessary to reduce the initial intensity one or more thicknesses of nickel foil were placed in the path of the beam between the second crystal and the sector.

The Method of the Stepped Wedge.—When the wedge method is used the transmission of each section of metal is calculated from its thickness and the known adsorption coefficient of the copper radiation. If there is any constituent of the beam harder than this it will pass through more easily and the relative intensities given by the wedge will differ from the calculated values, the ratio of the greater to the less being smaller than it should be.

When the beam had been reflected from a single calcite crystal no gradation could be seen on the sections of film under the thicker parts of the wedge. The intensity of the background close to the line was still 4 per cent. of that within it but the main cause of the lack of gradation was that these elements of the general radiation which have wavelengths of $\lambda/2$ and $\lambda/3$ ($\lambda = 1.54 \text{ \AA.}$) are selectively reflected by the calcite crystal. Hence to use the wedge method it was necessary to reflect from two crystals in succession.

Since it is impossible to prevent the reflection of radiation of wavelength $\lambda/2$, the metal of which the wedge is made (and of any other absorbing screen in the path of the beam) must be so chosen that the harder element is at least not preferentially transmitted. Nickel is the only metal that absorbs the ray of $1.54/2 \text{ \AA.}$ more than that of 1.54 \AA. and can be obtained in sufficiently permeable sheets. The step-wedges were made by cutting strips of pure electrolytic nickel foil 6 cm. long and laying them on each other so that eight longitudinal steps each 2.5 mm. wide were formed, each one being higher than the last by one or two layers of the foil. The thickness of the foil (0.00890 mm.) was found by means of an optical lever devised for the measurement of film thickness.⁹ The density was determined with all proper precautions and found to be 8.84. The percentage transmissions for the several steps of each wedge were calculated from these values of thickness and density and from the most recent value of the mass-absorption coefficient (μ/ρ) of nickel for $\text{Cu}\alpha$ radiation, given by the Braggs,¹⁰ and are indicated with sufficient precision by the graphs.

If the cube roots of the absorption coefficients (μ/ρ) of nickel given by the Braggs are plotted as ordinates against the appropriate wavelengths of the K series as abscissæ, a graph is obtained which consists of two straight lines sloping steeply downwards towards lower wavelengths. On one side of the absorption limit for nickel ($\lambda = 1.484$) we find μ/ρ for the characteristic α line of copper ($\lambda = 1.54 \text{ \AA.}$) is 49.2 but on the other side, for the octave of this ($\lambda = 0.77 \text{ \AA.}$) μ/ρ is 59.3. If we follow the graph downwards below $\lambda = 0.77$, we find that at $\lambda = 0.72$ the absorption coefficient has decreased to 49.2. When λ is $1.54/3 \text{ \AA.}$, μ/ρ is only 19.24. This means that there will be relatively rather less of the constituent of half the required wavelength after passing through the nickel but considerably more of that of one-third. This effect must occur with most other materials, whether elements or compounds, which are used to absorb unwanted harder radiation. It is a point frequently overlooked that there

⁹ Jones and Miles, *Trans. Soc. Chem. Ind.*, 1933, 52, 251.

¹⁰ Bragg, *The Crystalline State*, Vol. I, 1933, 325.

must be a lower limit of wavelength for the preferential absorption and that below this the result will be the reverse of desirable.

After two successive reflections the $\lambda/2$ constituent must be very weak and that of $\lambda/3$ much weaker since its reflection is one of the third order, but suppose as much as 1 per cent. of the latter were present.* After passing through all the ten layers of foil in the wedge (0.0890 mm.) the relative amounts would be 2.1 (λ) and 0.221 ($\lambda/3$) instead of 100 (λ) and 1.0 ($\lambda/3$). This would not be a very obvious cause of error, and for the thinner parts of the wedge it would be even less considerable.

The films were developed for five minutes at 18° C., suspended vertically in a large excess of the developer, the instructions of the makers being strictly carried out.

Discussion of the Moll Type of Photometer.—For most of the published work on the sensitivity of X-ray film the Moll micro-photometer has been used and the density has generally been defined as $\log_{10} (d_0/d)$, d_0 being the galvanometer deflection when light passing through the unexposed developed plate falls on the thermopile and d that when the blackened film is substituted. Occasionally the photometer has been calibrated in terms of the photometric densities determined by one of the instruments designed to deal with comparatively large areas of photographic plates. Although the densities determined in this way and by the Moll microphotometer do not generally differ very much the comparison should be unnecessary, for there seems to be no reason why the standard of density which is provided by the Moll instrument itself, or by any other which works with directly transmitted light, and has otherwise the necessary characteristics, should not be adopted in microphotometry.

Tests were made first of all with a micrometer slit between lamp and film to make sure that the deflection of the galvanometer beam was strictly proportional to the intensity of the light falling on the thermopile. When the distance between the galvanometer-mirror and the record was 100 cm. and the greatest deflection was 10 cm., the proportionality was exact.

The optical sequence which is commonly used with the standard instrument is the following: lamp, condensing lens, micrometer-slit, apochromatic condenser, film, objective, thermopile. Moll¹¹ stated that the defining slit between film and lamp was necessary to prevent the disturbing effect of scattering by excess light on the film, but it is difficult to see why the accuracy should be inferior if the slit before the film is removed and that on the face of the thermopile is alone used to define the area of film from which light is received. The second method appears, in fact, to be equally accurate and has the great advantage of allowing more light

to pass, so that dense films can be much more readily dealt with.

To examine this second method of working, an arrangement of lenses was found which allowed of the first slit being removed at will so that a density could be determined by both methods successively. A lens of 16 mm focal

Method.	1.	2.	1.	2.
Thermopile slit .	Open.	Closed.	Open.	Closed.
Density .	.067	.065	.729	.732
	.148	.147	1.008	1.013
	.224	.223	1.278	1.256
	.506	.505	1.524	1.518
	.515	.518	1.536	1.524
	—	—	1.972	2.028

length was substituted for the Zeiss objective and one of about 60 mm. focal length for the Zeiss condenser. The thermopile slit was closed to 0.30 mm. to receive only one-third of the breadth of the image of the

* Robinson (*Proc. Roy. Soc.*, 1933, 142, 422) found that the unwanted radiation from a single rock-salt crystal was about 1.6 per cent. of the whole and contained mainly the $\lambda/2$ element.

¹¹ Moll, *Proc. Physical Soc.*, 1921, 33, 207.

lamp by the second method; it was opened to 1.3 mm. to receive the whole of the image by the first method. A series of pairs of density determinations was then made by the two methods using for each pair an exactly marked area of the film. The results are given on opposite page.

Excepting one reading the agreement is all that can be expected. The second method can therefore be relied on as well as the first to give an accurate indication of the density of directly transmitted light. In what remains to be described the second method was used exclusively.

The Determination of Density.—On each film the unreduced line was divided with a fine pen into sections corresponding to those of the reduced line. A small area just large enough to include the image of the

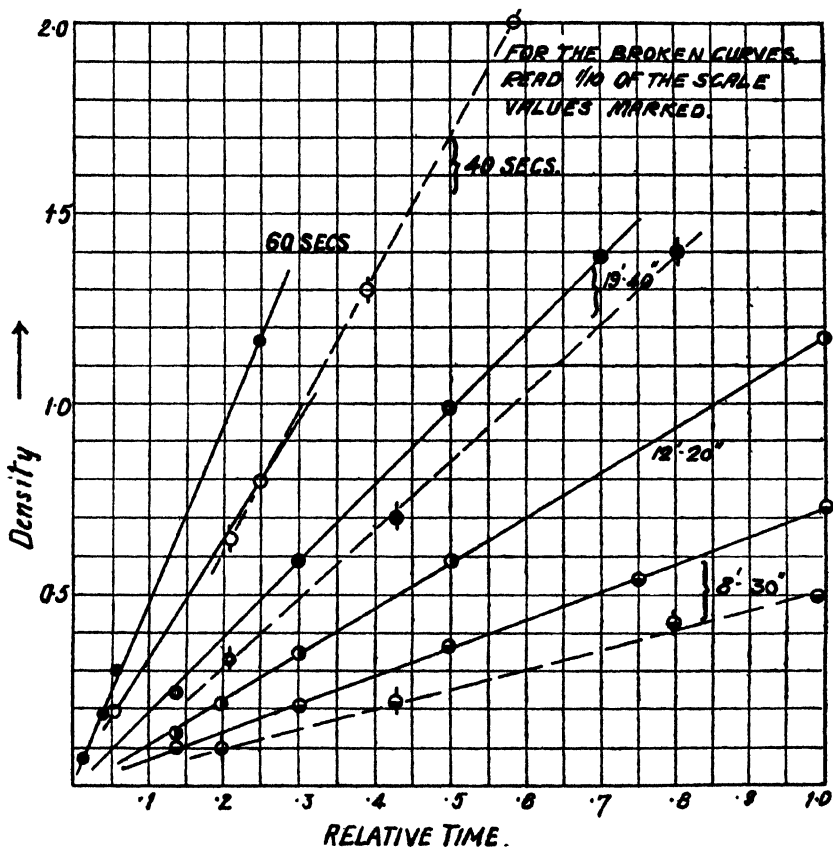


FIG. 1.—4—D Curves for Laue Film (Sector Method) 40-1180 Seconds.

photometer lamp was marked with ink on the clear film between the two lines. The readings corresponding to this area and to zero were first taken. Then the minimum deflections from all the sections of both lines were read and immediately after each one, if the density of the section was 0.5 or less, another reading was taken of the adjacent clear plate, but if it was more than 0.5, the zero was taken instead. Finally the deflection of the zero and of the marked area of clear plate were recorded once more to make sure that the emission of the lamp had been constant. When this procedure was not rigidly carried out errors were likely to be caused by variation in the photometer or by local differences in the sensitivity of the film.

The determined densities were then corrected for variation in initial

intensity of the beam by means of a series of numerical factors representing the densities of the sections of the unreduced line relative to one of them, as already described in the first paragraph under "Experimental".

Results.

The final results are given in the form of graphs. In order to exhibit more clearly any curvature in the graph near the origin which might indicate a threshold effect the plan has been adopted in most cases of plotting each series in two ranges, one on a scale ten times that of the other. The graphs of Fig. 1 were obtained by the use of sector wheels and represent

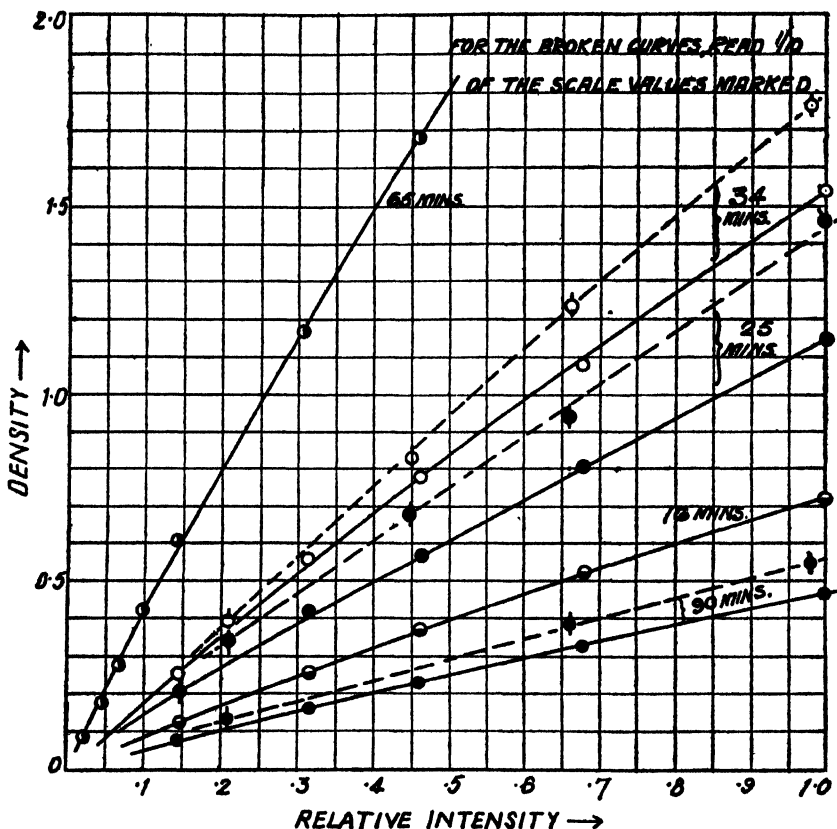


FIG. 2.—I-D Curves for Laue Film (Wedge Method).

the relation of density to time of exposure for various constant intensities. Those of Fig. 2 represent the results of the exposures with the nickel step-wedge and are more closely relevant to ordinary practice because the relation they display is that between density and intensity for various times, constant for each set but varying among themselves from sixteen to ninety minutes.

In neither case is there any evidence of a threshold. The graphs of both sets are nearly but not quite straight lines. The curvature near the origin is most clearly seen from the relative positions of the small-scale graphs drawn in continuous line and the large scale graphs in broken line. For the sector results the broken line has a smaller slope than the continuous

line of which it represents the initial part. The curve as a whole must therefore be slightly convex to the axis of intensity. The broken lines of the graphs of the wedge results, on the other hand, have the greater slope so that these curves are concave to the intensity axis. Here the concavity can be seen without any special method of plotting. The curvature in either case is small. The relation between density and intensity is much more nearly linear than Bouwers found it to be; improvements in the manufacture of X-ray film are doubtless responsible for this.

The curvature of the sector graphs is so slight that the error in the estimation of intensities up to and even over 1.0 on the basis of a linear connection with time of exposure would be inappreciable. What is desirable in practice, however, is nearly always a linear relation between density and intensity for constant time. When we consider the results of the wedge method, which really represents the required practical conditions, the linear connection is seen to hold less closely than before. In estimating the error which would arise in a series of density measurements, judging by the wedge results, we may in the first place restrict ourselves to a maximum density of 1.0, for values higher than this cannot be found very precisely. If the intensity producing this density (or the highest density shown by a graph in case it does not extend to $D = 1.0$) is taken as unity and the relative intensity giving rise to half this density is found, assuming the linear relation instead of that shown by the graphs, the error can be at the most 0.04 or 4 per cent. of the highest density measured.

In view of the many difficulties both in the measurement and application of X-ray intensities such an error will not be very serious in most classes of work, but it is nevertheless rather unsatisfactory that the two methods of film-calibration should give results differing in this way. To explain the difference there are alternative possibilities. If both sets of results are reliable then density is more nearly proportional to time than to intensity. There seems to be nothing impossible in this. On the other hand some error may have crept into the experimental work.

In both methods the difficulties of measuring densities of lines and of compensating for the unevenness of the initial beam are considerable, but the wedge method is for other reasons the more troublesome of the two. The effect of harder elements of radiation has been discussed; even with elaborate precautions it is not easy to be certain of excluding them. The thickness and density of the metal are involved and finally the calculation is dependent on previous knowledge of the absorption coefficient of nickel. The available values of this are (μ/ρ): 47.5 (Allen),¹² 47.3 (Martin and Lang),⁸ 45.7 (Intl. Critical Tables),¹³ and 49.2 (Bragg).¹⁰ Of these the last given is the most recent value and has therefore been accepted, although none of the details of the determinations have been published. In none is the purity of the metal very certain (impure nickel would probably have a higher absorption), and it seems otherwise likely that the method by which any of these values of the coefficient has been obtained is no more accurate than the procedure in which it has been used in this work.

Therefore in conclusion it may be said that X-ray intensity and density of blackening (measured by the direct transmission of light as distinct from scattering) may be taken to be proportional up to densities of 1.0. The error involved in this will not be more than 4 per cent. of the highest density measured, judging from one set of calibrations and much less judging from another. The method used for the set showing the greater divergence, has so many sources of slight inaccuracy that the departure of 4 per cent. from linearity is probably an over-estimate.

¹² Allen, *Physical Review*, 1906, 28, 907.

¹³ *International Critical Tables*, VI., 1929.

Conclusion.

The density of blackening of Agfa-Laue film by characteristic copper radiation may be taken to be proportional to the X-ray intensity up to a density of 1.0. The error involved in this is at the most 4 per cent. of the highest density measured. There is no evidence of threshold effect.

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*The Nobel Laboratories,
Ardeer.*

ELECTRODEPOSITION OF TIN ALLOYS FROM ALKALINE STANNATE BATHS.

BY R. G. MONK and H. J. T. ELLINGHAM.

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The electrodeposition of copper-tin alloys (bronze plating) has been studied by several investigators, and more recently the co-deposition of lead and tin has received some attention. For the latter, acid fluoborate or fluosilicate baths, similar to those which had been employed more particularly for the electrodeposition of lead, have been recommended.¹ For bronze plating, however, the types of bath developed have been based on those employed for the deposition of tin. Thus, solutions of the complex oxalates were widely favoured.² Comparatively little attention has been given, however, to the possibilities of co-depositing other metals with tin, or of adapting more modern types of tin plating bath to the deposition of alloys.

Very varied types of bath have been investigated in the attempt to obtain smooth, coherent electrodeposits of tin. It is, however, only in recent years that any notable fields of application for electrodeposited coatings of the metal have been opened up, and an effective stimulus given to the development of practical tin plating baths. Of the earlier types of bath, only a few have become established in modern practice. Thus, an acidified stannous sulphate solution with an addition of products of the sulphonation of phenols to suppress crystal growth³ seems to be the most successful bath of the simple stannous salt type; whilst alkaline stannite or stannate solutions survive as the chief representatives of baths in which the tin is present essentially as part of the anion. Whatever be the relative merits of these two general types of bath for the electrodeposition of tin, it is evident that the alkaline type should be much more readily adaptable to the deposition of alloys owing to the greater range of possible variation of the deposition potential of tin from such solutions.

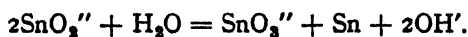
¹ Blum and Hazing, *Trans. Amer. Electrochem. Soc.*, 1921, 40, 287; Speichert, *Canadian Patent* 269480, 1927.

² Curry, *J. Physic. Chem.*, 1906, 10, 515; Treadwell and Beckh, *Z. Elektrochem.*, 1915, 21, 374; Mathers and Sowder, *Trans. Amer. Electrochem. Soc.*, 1920, 37, 525.

³ Mathers, *Trans. Amer. Electrochem. Soc.*, 1924, 45, 449; Foerster and collaborators, *Z. Elektrochem.*, 1926, 32, 525; 1929, 35, 409; 1930, 36, 901.

For some time it appeared that a stannite solution, possibly containing cyanide and certainly requiring an addition agent such as dextrose, peptone or glue, would turn out to be the most satisfactory alkaline bath for the deposition of tin;⁴ and a stannite-zincate bath with sulphonated castor oil as addition agent has been proposed for the deposition of tin-zinc alloys.⁵ During the last few years, however, notable advances have been made in the use of stannate baths, and this type of bath has already largely displaced the stannite type for the electrodeposition of tin in technical practice.

Although reference was made to stannate baths in very early times, it was not until 1911 that Naef showed the importance of keeping the solution free from stannite, since even small traces of the latter give rise to rough or coarsely crystalline deposits.⁶ This effect may be largely attributed to the tendency of stannite to decompose spontaneously with precipitation of metallic tin:



Some years elapsed before the importance of this point was realised, but eventually alkaline baths in which the tin was maintained in the quadrivalent state by addition of oxidising agents were developed.⁷ In Oplinger's process, which is in technical operation in the U.S.A., periodic additions of hydrogen peroxide or sodium perborate are made to a sodium stannate solution containing sodium acetate: tin anodes are employed. It has been shown recently, however, by Hothersall, Clarke and Macnaughtan⁸ that by the use of insoluble (nickel) anodes, tin can be maintained in the stannate condition without additions of oxidising agents, and control of the deposition process is thereby simplified. They recommend a solution containing 85 g. of tin (entirely as sodium stannate) and 15-20 g. of free sodium hydroxide per litre, operated at 70°-75° C. with current densities up to 6 (preferably 1.5-2) amp./sq. dm. Satisfactory deposits of any desired thickness may be obtained under these conditions; and, although the stannate content of the solution naturally falls during operation, the bath is readily regenerated by electrolysis with soluble tin anodes and insoluble nickel anodes, between which the current is divided in suitable proportion.

So far, little attention has been given to the deposition of alloys from alkaline stannate baths. For copper-tin alloys, however, Mathers and Sowder² recommended a solution prepared from ammonium stannichloride, potassium cuprocyanide, potassium hydroxide and free cyanide, operated at 40°-50°; and a bath prepared from sodium stannate, copper cyanide, sodium hydroxide and cyanide has also been specified.⁹ A stannate-aurocyanide bath for the electrodeposition of "white gold" has been proposed.¹⁰

In view of the importance of the above-mentioned recent developments in the deposition of tin from stannate baths, it seemed of interest

⁴ Cf. Wright, *J. Electrodep. Tech. Soc.*, 1932, 7, 103.

⁵ Thompson and Patten, *U.S. Patent* 1876156, 1932.

⁶ *Dissertation, Dresden*, 1911; Foerster, *Elektrochemie wässeriger Lösungen*, 1922, p. 184.

⁷ Siemens und Halske A.G., *Brit. Patent* 286673, 1928; Proctor, *Metal Ind. (N.Y.)*, 1929, 27, 267; Oplinger, *ibid.*, 1931, 29, 529; Wernlund and Oplinger, *U.S. Patent* 1919000, 1933.

⁸ *J. Electrodep. Tech. Soc.*, 1934, 9, 101.

⁹ City Auto Stamping Co., *Brit. Patents* 409001, 412277, 1932.

¹⁰ Kersten, *U.S. Patents* 1905105-6, 1933.

to investigate the possibilities of depositing tin alloys from baths of this type under conditions similar to those shown by Hothersall, Clarke and Macnaughtan to be most satisfactory for the production of pure tin deposits. Moreover, although the value of electrodeposited tin coatings on other metals for protecting the latter against corrosion is being increasingly recognised, the extreme softness of tin limits its application to conditions not involving exposure to appreciable abrasive action. For some purposes it would obviously be desirable to be able to obtain deposits having the corrosion resisting properties of tin coupled with a much greater resistance to wear, and it seemed probable that some electrodeposited tin alloys might be of value in these respects.

The present communication deals with a preliminary study of the electrodeposition of tin-nickel and tin-antimony alloys from hot alkaline stannate baths, with special reference to the dependence of the composition and properties of the deposits on the bath composition and conditions of electrolysis.

Electrodeposition of Tin-nickel Alloys.

The choice of a nickel salt to be added to the alkaline stannate bath is obviously limited to complex salts which are not appreciably decomposed by hot alkali. Nickelocyanides of the alkali metals naturally suggested themselves, and the baths actually employed throughout the present work were made up by addition of pure potassium nickelocyanide to the alkaline stannate solution.

Experimental Procedure.

Preparation of Sodium Stannate Solution.—Concentrated sodium stannate solutions were prepared by anodic dissolution of tin in sodium hydroxide solution at about 70° C., the stannite first formed being simultaneously oxidised at an insoluble anode, as proposed by Hothersall, Clarke and Macnaughtan.⁸ The electrolysis circuit was arranged so that the current entering the solution could be divided in any desired proportion between an insoluble anode of nickel gauze and a composite soluble anode consisting of slabs of cast "Chempur" tin. The cathode, also of nickel gauze, was contained in a wide glass tube, the lower end of which was plugged with asbestos wool pressed down so as to form an effective diaphragm separating the catholyte from the rest of the solution. The current through the insoluble anode was adjusted to about twice that through the tin anodes, and the current density at the latter was set initially at about 2 amp./sq. dm. Owing to the increasing tendency for tin to go passive as the concentration of free alkali falls, this current density had to be decreased progressively during electrolysis towards a final value of about 0.2 amp./sq. dm. The initial concentration of sodium hydroxide was chosen so that when the required amount of tin had dissolved the concentration of free alkali had fallen to 0.3-0.4 *N*.

The tin content of the stannate solutions was determined by the method of Evans,¹¹ and the free sodium hydroxide by the method described by Hothersall, Clarke and Macnaughtan.⁸ Total alkali (including sodium hydroxide, carbonate and stannate) was determined by titration with hydrochloric acid, using methyl orange as indicator. The sodium carbonate content was obtained by difference, assuming that all the tin was present as Na_2SnO_3 .

Apparatus and General Conditions of Electrolysis.—The electrolysis cell consisted of a 3-litre beaker around which was wrapped copper gauze covered with a layer of asbestos paper, over which was wound

¹¹ *Analyst*, 1931, 56, 171.

nichrome wire to form a heating coil: the whole was then lagged with asbestos. The current through the heating coil was adjusted so as to maintain the solution (about 2 litres) at 70°-75° (usually 70°-72°). The solution was stirred by an electrically-driven glass stirrer.

Copper cathodes were used throughout the present work. The surface was first cleaned by rubbing with metal polish, then degreased by cathodic treatment in caustic soda solution, and, after washing with distilled water, transferred immediately to the plating bath.

Rectangular copper plates, 13 cm. \times 2 cm., were commonly used as cathodes. By means of adjustable clamps supported from the ebonite lid of the electrolysis cell, two such plates could be mounted edge to edge in the same vertical plane forming a composite cathode, and anodes of somewhat larger area arranged on either side of the latter, plane-parallel to and equi-distant from its two surfaces. In some cases copper discs were used as cathodes. Each disc was mounted in a special holder designed so as to make electrical contact all round the edge of the disc, and set up in a similar fashion between two anodes.

In preliminary experiments flat plates of gas carbon were employed as anodes in order to avoid any possibility of the bath becoming contaminated with any metal which might be cathodically deposited. These plates were, however, gradually disintegrated and corroded in the hot alkaline solution which became dark brown in colour. In all subsequent work, sheets of nickel gauze were used as anodes. These were only slightly attacked, even in solutions containing notable amounts of free cyanide. Thus, with 5 g. of free cyanide per litre the current efficiency of anodic dissolution was only about 1 per cent.

Owing to the fact that the chemical equivalent of tin in the quadrivalent state (29.7) is very nearly equal to that of nickel (29.34), the current efficiency of metal deposition can be determined with sufficient accuracy for present purposes from the increase in weight of the cathode, the current strength and the time of electrolysis.

Analysis of Deposits.—Hot dilute hydrochloric acid had to be employed to dissolve the deposits for analysis, and, since this attacked the basis metal to some extent, the resulting solutions always contained copper, which interferes seriously with the determination of tin and nickel. After trying out several methods, the following procedure was adopted for the determination of the percentage of nickel in the deposits.

The solution obtained by dissolving a deposit of known weight (usually about 0.1 g.) in dilute hydrochloric acid was treated with bromine water to oxidise tin to the stannic condition, and then nearly neutralised with ammonia. The warm solution was saturated with sulphur dioxide, and copper precipitated as thiocyanate. After standing for a few hours, the precipitate was filtered off and the filtrate evaporated to a small bulk. Excess of thiocyanate was decomposed with bromine and excess of the latter removed by boiling. After adding a few grams of citric acid to prevent precipitation of tin on neutralising with ammonia, nickel was determined in the usual way as the glyoxime.

Experimental Results.

Preliminary experiments carried out with a simple sodium stannate—potassium nickelocyanide bath containing 40 g. of tin and 2 g. of nickel per litre yielded dark but lustrous deposits at very low current efficiencies (below 20 per cent.). During electrolysis, some decomposition of the nickelocyanide occurred with formation of a green slime, especially on the anodes. This was found to be prevented, however, by addition of potassium cyanide, and in all further work baths containing 5 g. of free potassium cyanide per litre were employed.

The effect of such addition of cyanide to the stannate bath itself was to restrict somewhat the range of current density over which high current

efficiencies of tin deposition could be attained. On the other hand, the free cyanide served to prevent to some extent the formation of the white sludge of insoluble tin compounds which otherwise tended to separate, especially on the heated walls of the containing vessel, during the operation of these small-scale baths in which, owing to the low ratio of the volume to the surface exposed to the air, any free caustic alkali was rapidly converted to carbonate. In the alloy deposition baths the maintenance of higher concentrations of free alkali, whether as hydroxide or carbonate, was undesirable, since it led to further decrease of current efficiency.

Composition of Deposits and Current Efficiency of Deposition.

The compositions of the baths used in the main experiments are indicated on Fig. 1, which shows how the nickel content of the deposit and the

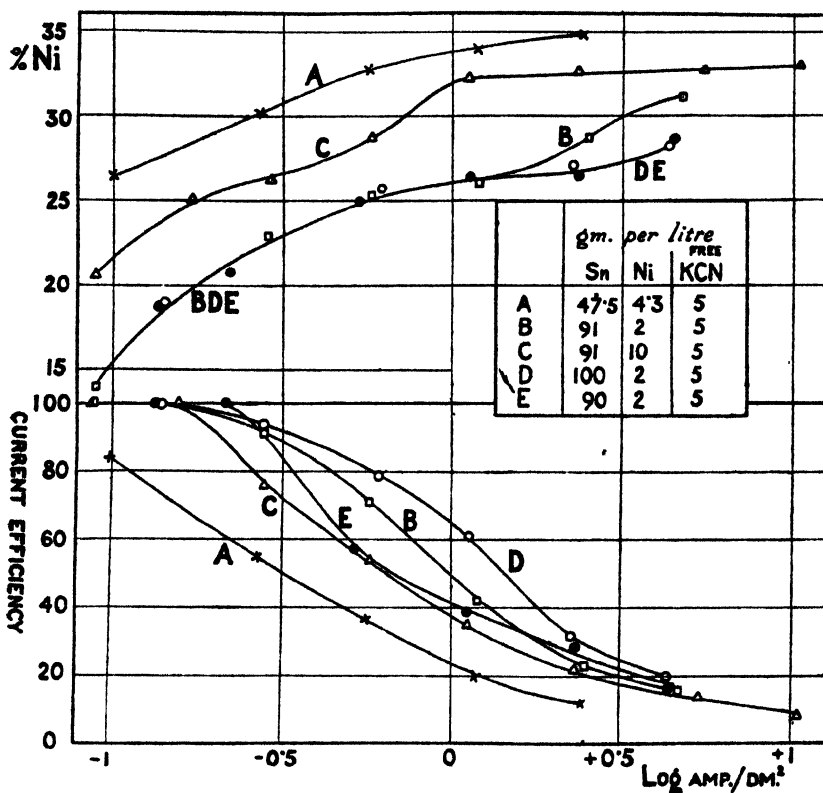


FIG. 1.

current efficiency of deposition vary with current density for these various solutions. In all cases the free alkali was 0.3-0.4 *N*, the major part of it being in the form of carbonate. Bath D was used for the preparation of a number of deposits, during which its tin concentration fell, partly owing to sludge formation, from 100 to 90 g./litre: after standing for some weeks the same solution, now described as bath E, was employed for the production of a further series of deposits.

In all the solutions an increase of current density causes the percentage of nickel in the deposit to increase, apparently towards an upper limiting value. With baths containing 90-100 g. of tin and 2 g. of nickel per litre, the nickel content of the deposit rises rapidly from about 15 per cent. at 0.1 amp./sq. dm., to nearly 25 per cent. at 0.5 amp./sq. dm., but only

reaches about 27 per cent. on further increase of current density to 2 amp./sq. dm. Increasing the nickel concentration of the bath to 10 g./litre raises the percentage of nickel in the deposit at any given current density by 4.5 units; while increasing nickel concentration to only 4.3 g./litre but lowering the tin concentration to 47.5 g./litre, raises this percentage by an average of about 8 units. At any given current density, therefore, the percentage of nickel in the deposit can be raised either by increasing the nickel concentration or by lowering the tin concentration of the bath, and alloy deposits ranging from about 15 to 35 per cent. of nickel were obtained from the solutions investigated.

Reference to the lower part of Fig. 1 shows, however, that the range of composition of deposits obtainable from these baths at reasonable current efficiency is much more restricted. With solutions containing 90 g. of tin and 2 g. of nickel per litre, current efficiencies approximating to 100 per cent. can be obtained up to about 0.2 amp./sq. dm., and 80 per cent. up to about 0.4 amp./sq. dm. The fall of current efficiency with increase of current density is made more rapid, however, either by increasing the nickel concentration or by decreasing the tin concentration of the bath. Thus, while a lower limit to the nickel content of the deposit is set only by the need for not working at too low a current density, an upper limit is set by the desirability of attaining a reasonably high current efficiency of deposition. In any case, it is advantageous that the tin concentration of the bath should be as high as possible, and the nickel concentration as low as can be maintained in practice, since the current density at which a deposit of specified nickel content can be produced at given current efficiency is as high as possible under these conditions. In bath D the concentrations of tin and nickel are respectively about as high and as low as are practicable. If 0.2 amp./sq. dm. be taken as the lowest current density, and 80 per cent. as the lowest current efficiency at which it is desirable to work, the limits of the composition of deposits obtainable are from about 20 per cent. to about 25 per cent. Ni. Within this range, the composition of the deposit is readily controlled, since it is not appreciably affected by small changes in bath composition or current density.

General Character and Properties of Deposits.—Sufficiently thin deposits of all alloys containing over 18 per cent. Ni were bright with a brilliant metallic lustre, but above a certain thickness their surface became matt and their appearance then resembled that of tin deposits obtained from the alkaline stannate bath. The only deposit prepared with a lower nickel content (about 14 per cent.)—from bath B at 0.09 amp./sq. dm.—was already matt at a thickness of 0.0001 inch. Deposits containing from 18 per cent. to about 28 per cent. of nickel remained bright up to thicknesses of nearly 0.0005 inch, and matt deposits free from notable surface irregularities were obtainable up to about 0.0007 inch. With over 30 per cent. of nickel, however, the surface became matt at thicknesses not much greater than 0.0002 inch, and at greater thicknesses nodular growths tended to develop.

With increasing nickel content, the lustre of the bright deposits tends to increase, but the colour becomes progressively darker. Increase of nickel content above about 26 per cent. causes a notable increase of brittleness. This may be connected with the fact, already noted, that the current efficiency of deposition falls off rapidly with increasing percentage of nickel in the deposit above about this value. Deposits containing over 30 per cent. of nickel readily flake off from the basis metal on bending the specimen or on treatment with hydrochloric acid, and those produced at higher current densities from baths A and C (at current efficiencies below 25 per cent.) tend to disintegrate during deposition. Deposits produced from baths B and D at about 1 amp./sq. dm. (about 26 per cent. Ni) were peculiar in exhibiting a tendency to form blisters when the preparation of thick layers was attempted: deposits obtained from these baths at higher or lower current densities were entirely free from this defect.

Experience of polishing the matt alloy deposits had indicated that they were all much harder than coatings of electrodeposited tin. Quantitative hardness tests on a number of alloy deposits of various compositions, about 0.0006 inch thick, on stout rectangular copper plates, were carried out by Dr. O'Neill and Mr. Kenneford at Manchester, using the "scratch" method recently developed by the former¹² for testing electrodeposited coatings. A few coatings of the same thickness deposited on copper discs were also tested for "wear resistance" by Mr. E. J. Daniels, using a method similar to that recently described by O. F. Hudson,¹³ and employing "precipitated chalk" as the abrasive.

Deposits containing between 22.4 per cent. and 25.2 per cent. Ni all gave scratch hardness values between 126 and 166, as compared with 21 for a deposit of pure tin obtained from the stannate bath at 1 amp./sq. dm. The hardness of these alloys is thus between 6 and 8 times that of pure tin. A deposit containing 24.2 per cent. Ni had a wear resistance also about seven times that of tin, taking the reciprocal of the loss of weight of the specimen per revolution in contact with the abrasive under standard conditions as a measure of the wear resistance. With increase of nickel content above about 25.5 per cent. however, the scratch hardness rises rapidly to values over twenty times that of tin, *e.g.*, to 460 at 28.3 per cent. Ni; but, owing to the simultaneous increase in brittleness, these deposits tend to crack in the neighbourhood of the scratch furrow, and the hardness values become uncertain. Moreover, the apparent decrease of wear resistance with increase of nickel content above about 26 per cent. is no doubt due to the increasing brittleness, for such deposits are readily cracked and small flakes of the alloy may be torn off under the action of the abrasive. It appears, therefore, that the only deposits obtainable from this type of bath which are likely to be of practical interest are those containing less than 26 per cent. of nickel.

The uniformity of the deposits, up to about 0.0006 inch at any rate, was shown by the fact that in the wear resistance tests the loss of weight in successive periods, each of 400 revolutions, remained reasonably constant until the deposit was practically worn away.

Although the deposits dissolve fairly readily in hot dilute or cold concentrated hydrochloric acid, they are less readily attacked by hot dilute sulphuric acid, and practically unattacked by hot or cold nitric acid of any concentration. Boiling with nitric acid results in the formation of a small quantity of metastannic acid, but the attack seems to cease after a time. In fact, in some cases, the copper basis metal can be dissolved away in nitric acid, leaving the alloy coating in fragments but quite unchanged in appearance.

Electrodeposition of Tin-antimony Alloys.

Of possible compounds of antimony which might be added to a stannate bath for the electrodeposition of tin-antimony alloys, sodium antimonite and antimonate naturally suggested themselves. Electrolysis of stannate baths containing even small concentrations of either of these salts yielded, however, dark powdery deposits with black outgrowths. Varying the current density over a wide range did not alter the character of the deposit, and no apparent beneficial results were obtained by addition of substances such as glue, resin or glucose to the bath. Addition of cyanide made the deposits lighter in colour and more metallic in appearance, but formation of black outgrowths still occurred after a short period of electrolysis.

In view of the fact that solutions of sulpho-salts have often been used for the electrodeposition of antimony, baths containing sodium thioantimonate (added as $\text{Na}_2\text{SbS}_4 \cdot 9\text{H}_2\text{O}$ —Schlippe's salt) were investigated.

The general procedure was the same as that adopted for the deposition

¹² *Trans. Farad. Soc.*, 1931, 27, 41.

¹³ *J. Inst. Metals*, 1933, 52, 101.

of tin-nickel alloys. Copper cathodes and nickel anodes were used as before.

Analysis of Deposits.—The tin-antimony deposits were not readily dissolved by hot or cold hydrochloric acid of any concentration, and, although they were rapidly attacked when potassium chlorate or bromine was added to the acid, this treatment caused some dissolution of the underlying copper: also when much antimony was present it tended to redeposit on the copper when the surface of the latter became exposed.

The procedure finally adopted was to prepare the deposits for analysis on thin copper foil and dissolve away this basis metal in nitric acid diluted with an equal volume of water. The insoluble residue of metastannic and antimonie acids thus obtained was filtered off, washed with dilute nitric acid, and freed from any remaining copper by the sulphide separation. The precipitated sulphides of antimony and tin were dissolved in hot concentrated hydrochloric acid, and the solution boiled to expel H_2S . Antimony was determined in an aliquot part of this solution by the volumetric bromate method, and tin in another part by the hypophosphite reduction method of Evans.¹¹ The latter determination appeared, however, to be unreliable for alloys rich in antimony.

Experimental Results.

The bath employed contained 89 g. of tin as sodium stannate, and 2 g. of antimony as sodium thioantimonate per litre, the free alkali concentration being about 0.1 N.

At 70°–75° C. coherent alloy deposits were obtained over a wide range of current density without accompanying hydrogen evolution. The following data show that deposits of almost any antimony content can be obtained from this bath by varying the current density, the antimony content *decreasing* with increase of current density:—

Current density (amp./sq. dm.)	0.1	0.24	0.5	1.0	2.0	4.4	9.1
Antimony content of deposit (per cent. Sb)	82.3	80	61.1	42.6	23.2	10.0	6.5

General Character and Properties of Deposits.—Deposits of high tin content have a dark coloured matt surface, but are fairly easily polished, and then have an appearance resembling that of polished tin coatings. With increasing antimony content the deposits become brighter but more brittle, and those very rich in antimony tend to flake off the cathode during deposition. Deposits rich in antimony which had merely been washed in water after removal from the bath tarnished readily. This could be prevented, however, by addition of hydrogen peroxide to the wash water, and was probably due to the action of H_2S formed by hydrolysis of the sulphide contained in an adhering film of electrolyte.

Deposits containing 10.0 per cent., 23.2 per cent. and 42.6 per cent. Sb all had scratch hardness values between 104 and 139, and were thus about 5–7 times as hard as electrodeposited tin. The alloy with only 6.5 per cent. Sb, however, had a scratch hardness of 39, which is less than twice that of tin. Alloys richer in antimony could not be obtained in layers of the requisite thickness (about 0.0005 inch) for carrying out hardness or wear resistance tests. All these antimony alloys, even those rich in tin, were very brittle, and the wear resistance test gave values which were actually less than that for pure tin deposits. It is very doubtful, therefore, if deposits of this type will be of any practical interest.

The evolution of a certain amount of H_2S when the deposits were treated with hydrochloric acid indicated the presence of sulphur, probably as antimony sulphide. Analysis showed that over 2 per cent. of sulphur was actually present in one of the tin-rich alloys, as well as in one containing 80 per cent. of antimony. The brittleness of this whole series of deposits may be largely due to this high sulphur content.

The authors express their thanks for valuable advice received from Mr. D. J. Macnaughtan, Director of Research to the International Tin Research and Development Council, at whose suggestion the investigation was undertaken; and one of us (R. G. M.) gratefully acknowledges the receipt of a grant from the abovementioned Council which enabled him to undertake the experimental work.

The authors also thank Dr. H. O'Neill, Mr. Kenneford and Mr. E. J. Daniels for carrying out hardness and wear resistance tests.

Summary.

Satisfactory electrodeposits of tin-nickel alloys containing up to about 25 per cent. Ni can be obtained at high current efficiencies from an alkaline bath at 70°-75° C. containing 90-100 g. of tin as sodium stannate, 2 g. of nickel as potassium nickelocyanide, and 5 g. of potassium cyanide per litre, using nickel anodes. Deposits containing 18-25 per cent. Ni, obtained at about 0.15-0.5 amp./sq. dm., remain bright up to a thickness of about 0.0005 inch, but then become matt: their hardness is about seven times that of electrodeposited tin. Deposits of higher nickel content, obtainable only at lower current efficiencies, are very much harder than the above, but owing to their notable brittleness their effective resistance to wear may be less.

Alloys containing tin and antimony in almost any proportion can be electrodeposited at practically 100 per cent. current efficiency from an alkaline stannate-thioantimonate bath at 70°-75° C. by suitable choice of current density (between 0.1 and 10 amp./sq. dm.). Only the alloys containing less than 50 per cent. Sb could be obtained as satisfactory deposits of thickness as great as 0.0005 inch, and even these deposits are very brittle so that, although notably harder than tin, their resistance to wear is liable to be very low.

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ON THE ADSORPTION THEORY OF THE ELECTROKINETIC POTENTIAL.

By A. MARCH.

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I.

The ζ -potential of colloidal particles is generally taken for the potential value on the boundary ("*Abreissfläche*") between the free liquid and the liquid adhering to the surface of a particle, *i.e.*, ζ is explained as a part of the whole (or ϵ -) potential. As the particle never loses its liquid coat, it can only react upon any influence with the ζ -potential, while the ϵ -potential, representing a property of its bare skin only, is doomed to inefficiency. Indeed, this interpretation seems to be confirmed by the fact that ζ is as a rule diminished by the addition of an electrolyte. One may see in this reaction an effect well known from Debye-Hückel's theory, according to which an increased concentration of the electrolyte diminishes the half-width of the ionic atmosphere. But

addition of KCl to an As_2S_3 -sol or of Na_2SO_4 to ferric oxide sols increases ζ instead of diminishing it. Moreover, it seems rather striking that electrolytes which in small concentrations diminish ζ , in greater concentrations are very often observed to invert the sign of ζ , which evidently cannot be explained on the assumption that the added electrolyte causes the ionic atmosphere to concentrate more and more into the space between the particle and the "*Abreissfläche*".

In addition to this, however, it is difficult to believe in the existence of an "*Abreissfläche*" defined sufficiently to accord with an exact value of ζ . If, as is likely, the liquid adhering to the particle is separated from the free liquid by a transition film which consists of several layers of molecules, a defined value of ζ could come about only, if the potential does not vary considerably within the transition film. That is possible, but it does not seem to be very likely. It is true that, according to the differential equation which applies to the potential ϕ , the value of ϕ in the "Debye-Hückel space" $\phi < \frac{kT}{e} = 0.03$ volt varies rather slowly,

diminishing to half the value only at a distance of about 10^{-6} cm at a concentration $N/1000$ of the electrolyte. But it varies very rapidly in the space $\phi > 0.03$ volt, to which ζ mostly belongs. For, from 0.03 volt the gradient of the ϕ -curve gets steeper and steeper, so that one layer of molecules may be sufficient to cause a considerable change of ϕ .

There is apparently only one way to overcome these difficulties resulting from the interpretation of ζ as a part of ϵ : the assumption that the two potential differences ζ and ϵ are independent of each other and have quite different origins. On approaching the surface of the particle the potential ϕ first goes up, for some reason or other, to the value ζ and beyond that, for some other reason, to ϵ , so that the total potential difference ϵ is composed of two parts, ζ and $\epsilon - \zeta$, which have nothing to do with each other.

Then the question which has to be answered first of all is: what is the origin of the ζ -potential?

There are not many possibilities which are to be taken into account. Evidently the potential is due to a force which, acting on the surface of the particle, separates the ions of the surrounding electrolyte or of the particle itself from one another, so that they build up a double layer. Of such forces we know only two. Either it is the same as that which splits up the molecules of an electrolyte into the ions, or the cause of the separation is an unequal adsorption of the ions by the surface of the particle.

Both possibilities have been considered, the former by W. Pauli and F. Valko, the latter especially by A. J. Rabinovitch and his pupils. But so long as one believes in a common origin of the ζ - and ϵ -potential, neither of the two conceptions proves satisfactory. The electrolytic theory is confronted with all the above-mentioned difficulties concerning the reaction of ζ upon an addition of an electrolyte; on the other hand, the adsorption theory is, indeed, able to explain potential differences of the order of ζ , but does not suffice, as will be shown, for potentials of the order of ϵ .

The latter objection is, however, of no significance, if we adopt the point of view that ζ and ϵ are independent quantities, each of which is to be interpreted for itself. Although the adsorption theory is certainly not sufficient for an explanation of the double layer as a whole, it nevertheless enables us to understand the value and behaviour of the ζ -potential.

Taken in this sense, the arguments Rabinovitch put forward at the last general discussion of the Faraday Society seem clear and convincing, and it may be worth while to investigate how far an exact theory can be built up on his speculations.

II.

Let us assume that a particle exerts an unequal adsorption on the ions of the surrounding electrolyte. If ϕ denotes the value of the electric potential at some point P and ψ^+ and ψ^- the adsorption potentials of a positive or negative ion, the number of the ions per cm.³ at P is given by :

$$n^+ = n_0 e^{-\frac{e\phi + \psi^+}{kT}}, \quad n^- = n_0 e^{-\frac{e\phi + \psi^-}{kT}}. \quad (1)$$

The expressions are, at least for large values of n^+ or n^- , not quite correct, since they indicate that the whole number of the ions adsorbed by the particle would increase proportionally to the concentration n_0 , which is certainly not true. The reason for this failure is that in (1) the volume of the ions is not taken into account; this volume is bound to influence the phenomena the more, the greater the number of the adsorbed ions is, and implies that n^+ and n^- are not proportional to n_0 but to n_0^α ($\alpha < 1$). However, as from the correct expressions for n^+ and n^- a very intricate differential equation for ϕ would result, on which a theory could hardly be based, we are forced to put up with the approximation (1), despite certain discrepancies with which we shall meet.

From (1) we obtain for Poisson's equation :

$$\Delta\phi = -\frac{4\pi}{D}\rho = \frac{4\pi n_0 e}{D} \left(e^{\frac{e\phi + \psi^-}{kT}} - e^{-\frac{e\phi + \psi^+}{kT}} \right), \quad (2)$$

D being the dielectric constant of the liquid.

For further consideration it is useful to substitute the adsorption potentials ψ^+ and ψ^- by two other quantities α and χ defined by :

$$\alpha = \frac{\psi^+ + \psi^-}{2}, \quad \chi = \frac{\psi^+ - \psi^-}{2}, \quad (3)$$

and, just as ψ^+ and ψ^- , representing certain functions of the distance from the surface. χ can evidently be taken for a measure of the difference of the forces with which the two kinds of the ions are adsorbed by the particle, and represents, therefore, exactly the quantity to which the formation of the double layer is due.

Expressing ψ^+ and ψ^- by α and χ , we obtain :

$$\psi^+ = \alpha + \chi, \quad \psi^- = \alpha - \chi,$$

so that (2) changes into :

$$\Delta\phi = \frac{4\pi n_0 e}{D} e^{\frac{\alpha}{kT}} \left(e^{\frac{e\phi - \chi}{kT}} - e^{-\frac{e\phi + \chi}{kT}} \right), \quad (4)$$

To solve this equation, let us make the simple assumption that ψ^+ and ψ^- are linear functions ascending towards the surface from zero within a space of the very small thickness Δ , i.e., we assume that the adsorption acts only up to the distance Δ from the surface, and that its forces are constant within this space. Then, according to (3), the function χ also

increases linearly along Δ from zero up to a certain value χ_m , which is positive in the case $\psi^+ > \psi^-$, i.e., if the adsorption of the positive ions outweighs that of the negative.

We will further assume that we are dealing with particles which are large enough for their surfaces to be considered as plane. Then ϕ gets a function of one co-ordinate only, *vis.*, the distance x from the plane wall, so that $\Delta\phi$ can be written $\frac{d^2\phi}{dx^2}$.

With the aid of these assumptions it is very easy to get an approximate idea about the course of the potential ϕ . In Fig. 1 the function $\frac{\chi}{\epsilon}$ is represented by the straight line which begins at the distance Δ from the wall and ends on the wall in the height $\frac{\chi_m}{\epsilon}$ above the x -axis. Now, in the case $\chi > 0$ (which is assumed in Fig. 1) the positive ions are favoured

in regard to the adsorption, and therefore the electric density ρ is bound to be positive in the immediate neighbourhood of the wall. This means that ϕ starts on the wall with a value as the density ρ is positive. But at greater distances x the density is negative, and therefore $\phi < \frac{\chi_m}{\epsilon}$ and remains $< \frac{\chi}{\epsilon}$ as far

for $\phi > \frac{\chi}{\epsilon}$. Thus, the curve representing the course of ϕ must intersect the straight line at a certain point S . This point where $(\epsilon\phi - \chi) = 0$, and therefore also $\rho = 0$ defines the boundary between the positive and the negative component of the double layer. On account of (4), the sign of $\frac{d^2\phi}{dx^2}$ is nega-

tive for $\rho > 0$. Accordingly the ϕ -curve is concave, seen from below, on the left side of S , convex on the right side, i.e., the course of the curve must be such as is suggested by Fig. 1.

It is evident from this figure that within the whole double layer ϕ remains below the value $\frac{\chi_m}{\epsilon}$. A closer examination of the adsorption forces will show that $\frac{\chi_m}{kT}$ in most cases fulfils the condition $\frac{\chi_m}{kT} < 1$.

This, together with $\phi < \frac{\chi_m}{\epsilon}$, allows us to develop the ϵ -powers in (4) and to integrate the equation for the "Debye-Hückel space" (which is characterised by $\alpha = \chi = 0$) by:

$$\phi = \phi_0 e^{-\kappa(x-\Delta)}, \quad K = \sqrt{\frac{8\pi n_0 \epsilon^2}{DkT}}, \quad (6)$$

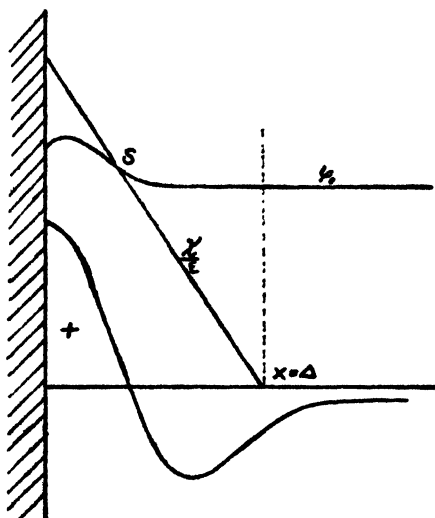


FIG. 1.

where ϕ_0 denotes the value of ϕ for $x = \Delta$. This solution holds only for the space outside Δ . Within Δ the quantities α and χ are different from zero, and it is therefore :

$$\frac{d^2\phi}{dx^2} = K^2 e^{\frac{\alpha}{kT}} \left(\phi - \frac{\chi}{\epsilon} \right), \quad (7)$$

The meaning of this equation may be made clear by means of Fig. 1, in which ϕ_0 is the height in which the ϕ -curve enters the adsorption space. Owing to the scale of the figure, the inclinaure of the tangent is very small for $x = \Delta$, so the curve is drawn there practically parallel to the x -axis. When one calculates the radius of curvature by means of the equation (7), it turns out that the ϕ curve keeps this parallelism at least half way to the wall. Only at $x = \frac{\Delta}{2}$ does the curvature become visible and cause the curve at first to rise a little and then, immediately in front of the wall, to sink again.

So ϕ remains within Δ always in close proximity to ϕ_0 . This value ϕ_0 which, in our opinion, represents the electrokinetic potential ζ , can be calculated by means of the condition that the double layer has to contain the same quantity of positive as of negative electric charge. According to (4) the electric density at some distance x is given by

$$\rho = \frac{2n_0\epsilon^2}{DkT} e^{\frac{\alpha}{kT}} \left(\phi - \frac{\chi}{\epsilon} \right),$$

i.e., we find the value of ρ belonging to a given x , by multiplying the difference of the ordinates between the ϕ - and the $\frac{\chi}{\epsilon}$ -curve by the

(variable) factor $\frac{2n_0\epsilon^2}{DkT} e^{\frac{\alpha}{kT}}$. In doing so, we obtain for ρ the lower curve of Fig. 1. The equilibrium of the charges demands that the two areas between the curve and the x -axis should be of the same size, and this is evidently only possible at a certain value of ϕ_0 . For it is ϕ_0 which determines the position of the intersection point S and therewith the size of the areas.

One sees at a glance that on account of the factor $e^{\frac{\alpha}{kT}}$, which increases rapidly towards the wall, S must lie very near to the wall, as otherwise the positive area with its high ordinates would outweigh the negative. This means that the ordinate of S is very near $= \frac{\chi_m}{\epsilon}$. But the ordinate of S is approximately $= \phi_0$, and so the result of our consideration is that ϕ_0 is practically $= \frac{\chi_m}{\epsilon}$. In view of the uncertainty of χ_m , a more accurate calculation of ϕ_0 would be of no value.

III.

So ϕ_0 turns out to be a quantity which depends only on the difference χ between the adsorption of the ions, whereas neither α nor Δ nor (which is particularly remarkable) the concentration n_0 have a noticeable influence on it. Let us further state that ϕ_0 represents a potential value which holds up to a considerable distance from the wall. For, according to Fig. 1, the potential varies within Δ very little, whereas it decreases

c being an individual constant which is of no interest for our investigation, R the gas constant, q the adsorption heat, and b van der Waals' volume correction. So from the theoretical standpoint the empirical relation (8) is incorrect, and its utility is confined to its practical conformity with (9) for those values of p which are generally used in experimental researches. We can make use of this to translate the representation (8) into the form (9), and to find out in this way the value of q . Thus, we put

$$1.539 \cdot p^{0.268} = \frac{cp}{p + \frac{RT}{b}e^{-\frac{q}{RT}}} = \frac{cp}{p + A} \left(A = \frac{RT}{b}e^{-\frac{q}{RT}} \right).$$

Applying this equation to two values p_1 and p_2 for which (8) holds, we obtain by division:

$$\left(\frac{p_1}{p_2} \right)^{0.268} = \frac{p_1 p_2 + A}{p_2 p_1 + A},$$

hence

$$A = \frac{p_2 - p_1 \left(\frac{p_1}{p_2} \right)^{-0.782}}{\left(\frac{p_1}{p_2} \right)^{-0.782} - 1}.$$

The measurements, represented by (8), extended over the range from $p_1 = 0.5$ up to $p_2 = 1.5$ mm. Hg. Thus we may choose for instance $p_1 = 0.5$ mm. Hg. $= 0.67 \times 10^8$ dyn, $p_2 = 1$ mm. Hg. $= 1.33 \times 10^8$ dyn. and get:

$$A = 1.33 \times 10^8 \frac{1 - 2^{0.782}}{2^{0.782} - 1} = 3.2 \times 10^8;$$

hence

$$q = RT(\ln RT - \ln(3.2 \times 10^8 b)) = \frac{RT}{0.434}(\log RT - 2 - \log(3.2b)).$$

As in this equation only the logarithm of b appears, the exact knowledge of b is not of great importance. We put it = 25, which approximately corresponds to the volume correction of H_2 or He. Then we obtain

$$q = RT \frac{1}{0.434}(\log(8.3 \times 3 \cdot 10^8) - \log 8000) \sim 15RT \sim 8900 \text{ calories},$$

which exactly corresponds to the order of magnitude measured by Krut on crystal violet. We may attribute to this method a considerable degree of certainty as an erroneous value of b is prevented by the logarithm from doing much harm.

Judging by the determined order of magnitude of $q = \psi_m$, one would estimate the possible difference $\psi_m^+ - \psi_m^-$ in the adsorption of the positive and negative ions at about 1000-2000 calories per mol. A difference of $\psi_m^+ - \psi_m^- = \frac{2000}{N}$ calories (N = Loschmidt's number)

would, according to the equation $\phi_0 \sim \frac{\chi_m}{\epsilon} = \frac{\psi_m^+ - \psi_m^-}{2\epsilon}$, bring about a

potential ϕ_0 of the amount $\phi_0 = \frac{1}{4.77 \times 10^{-10}} \cdot \frac{4.2 \times 10^7}{0.6 \times 10^{24}} 300 \text{ volts} = 0.045$ volt, i.e., just the amount which is usually met with for the ζ -potential. Essentially higher potentials are not likely to form; much less could we

think of the possibility of explaining the total potential difference ϵ (the order of which is probably 1 volt) by an unequal adsorption of the ions. That would demand adsorption potentials at least ten times greater than they are likely to be. This is the reason why we cannot believe in an adsorption theory of the whole ϵ -potential, and must insist on a theory that considers the ζ -potential as independent of ϵ .

But even then a difficulty remains. We have previously seen that ζ -values below 0.03 volt are comparatively rare, ζ in most cases being between about 0.03 and 0.07 volt. Does this fact mean a corresponding rarity of adsorption differences below 1500 calories? As this can hardly be assumed, we imagine that another field, originating from the ϵ -layer, is superposed on the field due to the unequal adsorption of the ions. Owing to the thermic agitation of the ions, this layer too, whatever its origin may be, will fade away relatively slowly in a "Debye-Hückel zone" characterised by $\phi < \frac{kT}{\epsilon}$. This zone superposes on the adsorption

layer a potential of about $\phi_1 = \frac{kT}{\epsilon} = \frac{1.3 \times 10^{-18} \times 300^2}{4.77 \times 10^{-10}} = 0.025$ volt,

so that on the whole a potential of the amount $\phi_0 + 0.025$ volt will come about there. Thus, an adsorption difference up to 2000 calories—as the difference is likely to be, on an average—will cause a ζ -potential of 0.025 up to 0.07 volt, provided that ϕ_0 and ϕ_1 are of the same sign. So we reach a complete agreement with experience, and can explain the rarity of ζ -values < 0.03 volt by the assumption that the sign of ϕ_1 is in most cases that of ϵ .

IV.

Let us proceed now to an investigation of the effect produced on ϕ_0 by the addition of another electrolyte. We will, as previously, put the

number of the adsorbed ions $= n_0 e^{\frac{\epsilon \phi_0 + \phi}{kT}}$, i.e., we shall again disregard the volume of the ions. That means that we shall treat the case of two substances in such a way as if the adsorption of the one substance would in no way (except by the electric potential ϕ , see below) interfere with that of the other. As is well known, such an additivity of adsorption does not really exist, as the molecules displace one another by their volume. Although, therefore, the following considerations may only be taken as a rough approximation, they will give at least a qualitative insight into the processes in question.

Let us then assume that two electrolytes 1 and 2 are present, both of which are adsorbed by the particles of the colloid. We shall use for the concentration, adsorption potentials, etc., of the one electrolyte the denotations introduced in II. and distinguish from them the corresponding quantities of the other electrolyte by adding an apostrophe to the symbols. The electric potential ϕ , of course, is to be excepted from this procedure as it is caused by both electrolytes together.

Again, a figure will help us to see at a glance what will happen. In Fig. 2 the functions $\frac{\chi}{\epsilon}$ and $\frac{\chi'}{\epsilon}$ of the two electrolytes are represented by the straight lines AB and $A'B'$. Both functions are supposed to be positive. The line denoted with ϕ is meant as a representation of the potential which would come about if the electrolyte 1 *alone* were present. ϕ determines together with $\frac{\chi}{\epsilon}$ two areas BCS and SAD . These

areas multiplied in the ordinates by the factor $\frac{2n_0e^3}{DkT}e^{\frac{\phi}{kT}}$ are, as we know, a measure for the positive or negative charge of the double layer, and the curve ϕ takes its course at such a height that the charges just balance each other. But once the other electrolyte is added, the equilibrium is disturbed because by the adsorption χ' an additional charge (corresponding to the area between ϕ_0 and χ') is called forth. Thus, if ϕ kept its height the negative charge would predominate in the double layer. For this reason the potential is bound to sink, say from ϕ_0 to $\bar{\phi}_0$. So the adsorption of the positive ions increases (from BCS to $BC'S'$), whereas at the same time the number of the negative adsorbed ions diminishes until the equilibrium between the charges is re-established.

Of course, the addition of another electrolyte may cause ϕ_0 to increase as well as to decrease. Which of the two possibilities will really happen depends not only on the course of χ and χ' , but also on the ratio of the

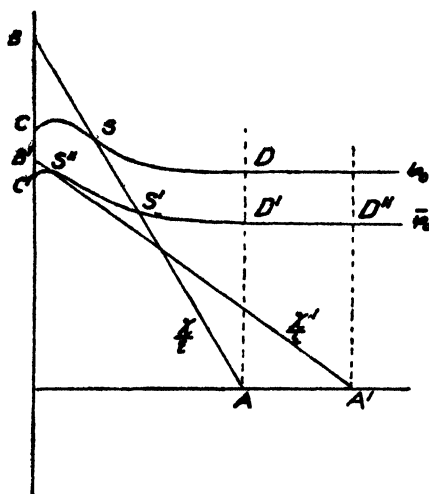


FIG. 2.

concentrations n_0 , n_0' , and on the quantities α and α' . Without any calculation we can only see that in the case of different signs of χ and χ' the amount of ϕ_0 is bound to diminish in any case. In the case of the same sign ϕ_0 will generally decrease if the terminal value χ_m of χ is greater than χ'_m . The fact that in most cases a decrease of ϕ_0 is observed is likely to be explained by pointing out that the majority of experiments refer to substances the ζ -potential of which is high. For such systems (with large values of χ_m) it is, of course, more probable that $\chi'_m < \chi_m$ than that $\chi'_m > \chi_m$. It has, however,

been mentioned already that there are many cases in which an increase of ϕ_0 has been ascertained.

Let us, further, with the help of the figure, make a phenomenon clear which is of great importance for the physics of colloids. When by the addition of the other electrolyte the potential ϕ_0 is diminished to $\bar{\phi}_0 < \phi_0$ (as is assumed in Fig. 2), the consequence is that more positive ions of the initial electrolyte are adsorbed, whereas at the same time the number of the adsorbed negative ions gets smaller. Thus a certain number of negative ions separate from the surface of the particles, flowing back into the intermicellar liquid. As a compensation, in order to equalise the increased positive charge, the surface adsorbs a certain number of negative ions of the added electrolyte. One has interpreted this process which has been called "exchange adsorption," as a displacement of the old ions by the new ones due to the stronger attraction exerted on the latter. Actually, the explanation of the process is not so simple. It may be that the original ions are more strongly adsorbed than the new

ones and, in spite of that, have to make room for the latter. The reason is that this is the only way to re-establish the equilibrium disturbed by the added electrolyte.

If the ions were uncharged, such a disturbance of the equilibrium would not come about at all, but the adsorptions would simply superpose on one another additively—provided that the volume of the ions can be neglected. The charge of the ions, however, makes this additivity impossible by imposing the condition on the adsorptions that the whole charge of the double layer must be zero. This condition entails that any additional adsorption is bound to alter the original one, and it is this alteration to which the phenomenon of exchange adsorption is due.

As long as one insists on regarding exchange adsorption as a mere replacement of less preferred ions for more favoured ones, one must assume that the exchange can take place only in equivalent quantities. A. J. Rabinovitch has emphasised that both theory and experiment are against such an equivalency, and we cannot but endorse his opinion. Let us once again look at the figure. When the potential sinks from ϕ_0 to $\bar{\phi}_0$ the ions of the original electrolyte are influenced in contrary ways. Whilst the number of the "charging" ions increases (from BCS to $BC'S'$) that of the "*Gegenionen*" diminishes from SAD to $S'AD'$. Thus, with the additional adsorption of the one kind of ions a *desorption* of the other is connected and we will denote the numbers of the ions that are adsorbed or given back to the intermicellar liquid by N_1 or N_2 . At the same time, a certain number, N_3 , of negative ions of the added electrolyte is adsorbed (area $S''AA'D''$). According to the requirement of equivalency this N_3 ought to be $= N_2$. But in fact the condition that just as much positive as negative charge is taken in by the layer, requires for the numbers N the equation $N_1\epsilon = (N_3 - N_2)\epsilon$, hence *not* $N_3 = N_2$ but $N_3 = N_2 + N_1 > N_2$. Thus the principle of equivalency does not hold, but it is to be supposed that more "*Gegenionen*" of the added electrolyte are consumed than are replaced by the ions detached from the particles. How far this consequence is in accordance with the experiments is, indeed, a question difficult to decide, on account of the fact that in most cases the balance of the exchange is falsified by the formation of insoluble salts. Nevertheless, the experimental investigations carried out by Rabinovitch and his pupils seem to leave no doubt that, at least in the majority of cases, the ions are not exchanged in equivalent quantities. For instance, it was found that on adding Ba salts to alkaline silica sols a considerable adsorption of Ba ions is connected with the replacement of a very small amount of H ions which conforms to our theoretical result that N_3 has to be $> N_2$.

Summary.

1. It has been pointed out that the facts can only be brought in accordance with a theory which considers the ϵ - and ζ -potential as independent quantities.
2. The course of the potential within a double layer due to an unequal adsorption of the ions has been examined. The result is a very simple connection between the value ϕ_0 to which the potential rises in the layer, and the difference of the adsorption potentials.
3. The order of magnitude of ψ is calculated from experiments on the adsorption of Cl-ions by Fe_2O_3 sols. The order we find in this way corresponds to that of ζ .

4. Also the way in which ϕ_0 reacts upon the addition of an electrolyte is quite that of ζ which accordingly, in all probability, must be interpreted as an adsorption effect.

5. The mechanism of the exchange adsorption is made clear by means of a figure which shows that the principle of equivalency does not hold for this process.

I have much pleasure in thanking the Imperial Chemical Industries, whose generosity enabled me to carry out this investigation.

ON THE USE OF DIRECT CURRENT IN THE MEASUREMENT OF ELECTROLYTIC CONDUCTANCE.

BY J. N. BRÖNSTED AND RALPH F. NIELSEN.

Received 14th August, 1935.

1. Introduction.

The usual alternating current method for determining the electric conductivity of solutions is well suited for the case of resistances of a moderate magnitude. In the case of large resistances or if a very high degree of precision is required elaborate precautions, however, must be taken to secure satisfactory results.¹

The present investigation was carried out in the endeavour to apply the direct current method to acid or basic solutions, eliminating the polarisation by using platinised hydrogen electrodes. The actual purpose was to develop a conductivity method for determining reaction velocity in alkaline solution. The result of this part of the work will be described elsewhere.

The method of using direct current for conductivity measurements is not new in principle. It has been tried by several previous investigators, and various means have been utilised to avoid polarisation, for instance calomel and mercurous sulphate electrodes,² and also hydrogen electrodes.³ The method, however, has not as yet received general attention, probably because it is usually believed that a very high degree of precision is not obtainable or because its advantages are not appreciated. These include, especially, simplicity as compared with the procedure necessary to obtain equal precision with alternating current. This is true particularly in the case of solutions of very low conductivity, where the accuracy of the measurements can be increased by the simple expedient of increasing the applied potential difference. The heating effect thus produced can be minimised because of the very short time during which the current must flow in order to test the bridge setting.

In previous measurements of this type, as far as we can determine, it has not been emphasised that no great precautions with the electrodes and electrode chambers are necessary. From the experience of the

¹ Cf. Washburn, *J. Am. Chem. Soc.*, 1913, **35**, 177; 1916, **38**, 2431; 1917, **39**, 235. Grinnel Jones and Josephs, *J. Am. Chem. Soc.*, 1928, **50**, 1049.

² Newberry, *J. Chem. Soc.*, 1918, **113**, 701; Eastman, *J. Am. Chem. Soc.*, 1920, **42**, 1648.

³ Marie and Noyes, *J. Am. Chem. Soc.*, 1921, **43**, 1095.

present investigators no special measures are necessary to determine the conductivity of an acid or basic solution with a similar accuracy to that obtainable in the case of a metallic conductor.

2. Apparatus and Procedure.

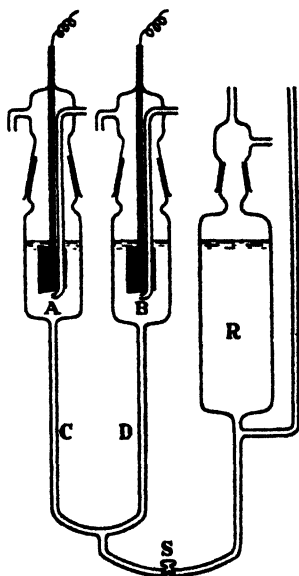
The resistance in the cell described below was determined by means of an accurate Wolf bridge with five dials and eight ratio coils, two each of 10, 100, 1000 and 10,000 ohms. The coils were all checked and calibration was found unnecessary.

As a current indicator the Zeiss "*Schleifengalvanometer*" with microscope was used. This instrument was chosen because of its short period and rapid response. The sensitivity was 2.4×10^{-7} volt per scale division and the resistance 7.3 ohms. In measuring a resistance of 10,000 ohms., that of the cell filled with tenth normal sulphuric acid, the setting could be determined to within one part in 100,000, using a 10 volt battery. In the case of the most dilute solutions a 50 volt battery was used.

The design of the conductivity cell used in our experiments is shown in the figure. It consisted of the two electrode chambers A and B, connected by the arms CD which had an internal diameter of about 6 mm. and a total length of about 50 cm. It was made of orange-stripe Jena glass and had been in use for aqueous solution about a year. The tube from the reservoir R to the stop cock S was a 1.2 mm. capillary. The electrodes were 2×3 cm. and the lower edge of each about 2 cm. above the bottom of the electrode compartment. Other details are apparent from the figure. It will be seen that nearly all the resistance is in the 6 mm. arms. Fresh solution can be run into these at any time from the reservoir. The cell was immersed in a bath of distilled water, the temperature of which was $25^\circ \pm 0.003$. For higher resistances than those studied here a bath of a non-conducting liquid would be preferable.

The electrodes were only lightly platinised. The solution to be measured was put into the reservoir after the cell had been thoroughly rinsed with the given solution. This was then forced into the arms of the cell by means of the hydrogen so that the electrodes were covered. No effect caused by the height of the solution above the electrodes could be detected, although there was a slight difference in the cell constant when they were not covered. Hydrogen was then bubbled over the electrodes until they were at the same potential, or so nearly the same that no appreciable deflection was observed when the galvanometer key was depressed. The effect of the flow of hydrogen on the cell constant was usually not measurable, being in any case far beyond the limits of other errors.

When making the measurements, the battery key was usually depressed just an instant ahead of the galvanometer key, the latter tapped quickly, and then both keys released. The current did not flow through the cell more than a quarter of a second at a time, in which time the heat effect is quite negligible. The electrodes were tested frequently for polarisation by depressing only the galvanometer key. In case of the 0.1 normal solutions using a 10 volt battery there was a slight polarisation, the presence of which, however, does not seriously affect the accuracy, because it is



possible to allow for the polarisation by alternately depressing both keys and the galvanometer key alone to give equal deflections. These were, in the worst case, only one or two scale divisions, the deflection produced by a change of less than one part in 10,000 in the dial setting. Determination of the resistance with an accuracy of 10^{-5} was thus not excluded, even in the presence of a slight polarisation.

Since the cell was filled from below with the solution from the reservoir, the walls were thoroughly rinsed and brought into equilibrium by the first portion of the solution. Readings were checked several times by running in fresh solution from the reservoir, forcing the old solution into the electrode compartments, and agreement was always obtained to about one part in 10,000. Since, as mentioned above, only a small part of the resistance is in the electrode compartments, a slight error in concentration in these does not affect the results, so long as no appreciable potential difference is set up.

3. Examples.

Measurements in the present part of the investigation were made with hydrochloric and sulphuric acid, using pure preparations and carefully adjusted concentrations. In the following table the observed results are compared with data taken from Int.

EQUIVALENT CONDUCTIVITIES OF HCl AND H_2SO_4 SOLUTIONS AT 25° C.

c.	Obs.	C.T.	S.
HCl	0.1	(389.8)	389.8
	0.05	397.7	397.8
	0.02	405.8	406.1
	0.01	411.3	411.1
	0.005	415.1	415.1
	0.002	419.0	419.2
	0.001	420.7	421.4
H_2SO_4	0.1	(250.8)	250.8
	0.05	272.5	272.6
	0.02	307.9	308.0
	0.01	336.4	336.4
	0.005	362.8	364.9
	0.002	389.9	390.3

Crit. Tables. The parentheses show the measurement from which the cell constant was taken. Since it is merely the purpose of this investigation to test the applicability and accuracy of the method, rather than to obtain data of the highest absolute precision obtainable by the method, independent values for the cell constants were not determined. The concentrations c of the solutions are given as equivalents per litre of solution at 25° C. Both the data of Shedlovsky⁴ and the recalculated older data are given for hydrochloric acid.

The data are given to one significant figure less than it was possible to determine the dial settings on the bridge. We believe that the observed values in each series are

within the limits of errors caused by inaccuracy in concentration, and that the slight discrepancies are not due to the method itself. The only case in which there is a considerable difference in the two series is at the concentration 0.005 H_2SO_4 . As we have checked our value repeatedly, and it fits better in a graphical representation of the data than the C. T.-value, we believe that there must be an error in the previous determinations at this concentration.

Summary.

1. The use of direct current, where applicable, is recommended as a substitute for alternating current for the accurate determination of conductivities of solutions.

2. Advantages of the method include simplicity of apparatus and procedure as compared with that necessary to obtain the degree of accuracy with alternating current, especially in the case of solutions with low conductivities.

⁴ Shedlovsky, *J. Am. Chem. Soc.*, 1932, 54, 1411.

3. A simple apparatus and procedure is described by which conductivities of acid and basic aqueous solutions may be determined with high accuracy. Examples are given for hydrochloric and sulphuric acid solutions ranging from 0.1 to 0.001 normal.

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REVIEWS OF BOOKS.

The Diffraction of Light, X-rays and Material Particles. By CHARLES F. MEYER. (Chicago: University of Chicago Press; Cambridge: at the University Press. Pp. xiv + 473, with 283 illustrations. Price 22s. 6d. net.)

Generations of both students and teachers have been accustomed to turn to their "Preston" or "Wood" when confronted with problems in diffraction; it may well be that this book will become part and parcel of college equipment in the future. It provides a welcome breath of fresh air, and yet, at the same time keeps some kind of hold upon the historical background. There is not a great deal which is new to be said about diffraction; nevertheless it is true that most treatments do little beyond going over the surface with a rake, whereas here the soil is fairly thoroughly ploughed.

The author has evidently been at considerable pains to make the classical theorems—and results—live in the mind of his reader, and in this he has been successful except in one or two instances wherein a bolder acceptance of higher mathematics would have helped: nobody is really impressed by stopping short, and being told, in effect, that such things are not for him.

All the usual problems are discussed, though considering the bulk of the volume, some are dismissed somewhat briefly. In dealing with the infra-red grating spectrometer, the need for a filtering system is very rightly stressed for fine-structure work. Calculation will readily reveal, however, that a much more delicate turning interval than one minute of arc is required: the present reviewer and his colleagues used a grating table some six times as refined as that several years ago, and much improvement has been achieved since then.

A very valuable reference is that to the efforts of Gerhardt (1926) to measure the diameters of very small particles (1.5×10^{-8} cms.) by a method analogous to Michelson's well-known "Star" arrangement. The advance of physical microscopy in recent years has been marked, largely due to the pressure of crystallography; these hints should be welcome to workers in such a field.

Some space towards the end is devoted to the diffraction of material particles, and there are several appendices. The text is good: one misprint occurs on page 151, but the sense is not destroyed.

Students may perhaps pause before spending over a pound upon a book dealing with (in a sense) so limited a subject, but University libraries will do well to have it easily accessible upon their shelves.

F. I. G. R.

The Theory of Atomic Collisions. By N. F. MOTT and H. S. W. MASSEY.
(Oxford: Clarendon Press. Pp. xv + 283. 17s. 6d.)

During recent years a new and valuable technique has been developed which provides information as to the shapes and sizes of molecules. It has thus become of great interest to chemists as well as physicists. This technique consists in the accurate control of beams of electrons and atoms and the measurement of their diffraction by gases or thin films. But this experimental development, while interesting in itself, would be of little practical importance if it were not for a corresponding advancement of the theoretical aspects of the subject. This book deals with recent progress in the theory of electron and atomic scattering. It is the first of its kind in this field and as such it is likely to prove important in stimulating further discoveries.

This is a scholarly book which will well repay study by those interested in Quantum Mechanics. The meaning of wave mechanics is made clear by many an illuminating passage, incidental to the main argument or application. There is a particularly interesting and well-written chapter on the interaction of two similar particles, which admirably illustrates the significance of symmetrical and anti-symmetrical wave functions and their relation to observation.

Among the important subjects dealt with in this book there are the theory of elastic scattering of electrons by atoms, the excitation of atoms by electrons, the diffraction of electrons by molecules and the collisions between heavy particles.

The authors have given in some detail the treatment of collisions between particles moving with relatively small velocities, and the methods there developed are likely soon to prove of importance in the study of chemical kinetics.

The reviewer has studied this book in some detail and has nothing but praise for the care and lucidity with which it has been written, and can confidently recommend it as an authoritative treatise on the subject of atomic collisions.

CORRIGENDUM.

Page 1220: Second paragraph, lines 6 to the end should be deleted and replaced by:—

annealed metal. This appears significant and suggests that interference with crystal growth, or inclusion of foreign matter, occurs under all conditions of deposition so far examined. It remains to be proved whether in soft deposits this hardening effect is entirely due to the presence of colloidal hydroxide in the film of liquid adjacent to the cathode, but if this is so, it may go far towards providing an explanation of the irreversibility of nickel deposition.

FREE RADICALS IN THE PHOTODISSOCIATION OF GASEOUS METAL-ALKYLS.

BY N. PRILESHAJEVA AND A. TEREININ.

Received 18th July, 1935.

In a previous paper from this laboratory, absorption spectra of the vapours of $\text{Hg}(\text{CH}_3)_2$ and $\text{Pb}(\text{C}_2\text{H}_5)_4$ were described.¹ Both compounds possess regions of continuous absorption beginning at about λ 2800 for $\text{Hg}(\text{CH}_3)_2$, and at λ 2700 for $\text{Pb}(\text{C}_2\text{H}_5)_4$ and stretching from these wavelengths towards the shorter ultra-violet. In addition, mercury dimethyl vapour exhibited a diffuse band spectrum situated between λ 2125 and λ 1965. The continuous absorption was ascribed to a photo-dissociation of these molecules with the liberation of a CH_3 or a C_2H_5 radical. It was assumed that the diffuseness of the band spectrum of $\text{Hg}(\text{CH}_3)_2$ was due to a predissociation, in which a splitting of the molecule into CH_3 and HgCH_3 occurred.

These results are in general accord with the recent work of Duncan and Murray,² and of Asundi, Bhasker Rao, and Samuel.³

Although much information as to elementary processes in gas molecules may be obtained from the absorption spectrum, the conclusions based on it are seldom unambiguous, especially when broad regions of continuous absorption are observed. Therefore to obtain an adequate interpretation of the process occurring under the action of light, other more direct methods are to be sought which should permit the detection of the products of dissociation before they react further.

One of these methods which is being extensively used in this laboratory, is the observation of the emission spectra of the products of the photo-dissociation. In the case of organo-metallic compounds this was successfully applied to CH_3HgHal vapours, for which the splitting into CH_3 and excited HgHal radicals was directly ascertained.¹ The

¹ Terenin and Prileshajeva, *J. Chem. Physics*, 1934, **2**, 441; *Acta Phys. Chim. U.R.S.S.*, 1935, **1**, 759.

² Duncan and Murray, *J. Chem. Physics*, 1934, **2**, 636.

³ Asundi, Bhasker Rao, and Samuel, *Proc. Ind. Acad. Sc.*, 1935, **1**, 542. These authors found in mercury dimethyl a nearly continuous region of absorption occupying exactly the same spectral range as the diffuse band spectrum observed by us. This is to be ascribed to the fact that we were working with a much longer absorbing column and a lower pressure of the vapour, which were both favourable to a better resolution of the spectrum. The feeble bands superposed on the continuum which were found by these authors may well have been overlooked by us, as the dispersion of our apparatus was small.

In this connection we should like to correct a statement in our previous paper that the molecules HgR_2 and ZnR_2 were to be regarded as linear. From the data of the Raman spectrum it is to be inferred that in the liquid state these molecules are *triangular* with a very obtuse apex angle, i.e. approaching a linear shape.

method is a very sensitive one, but can be applied only when the products possess readily excitable spectra with relatively low-lying energy levels. When the photo-dissociation leads to non-emitting particles, this method is not applicable.

Another very promising method, especially suited to the study of organic compounds, is based on the fact that metal deposits react with free alkyl radicals and are removed in a gas stream, in the form of volatile organo-metallic compounds.⁴ This method is now being extensively used to study the thermal decomposition of various organic molecules.⁵ Its application to the investigation of photochemical reactions was desirable.

Recently such a method has been successfully applied by Pearson⁶ to the study of the photo-decomposition of carbonyl compounds. He proved that free radicals are produced during the decomposition of ketones by light, in agreement with the view advanced previously by Norrish.⁷

Some time ago we began a similar investigation on the vapours of organo-metallic compounds, as a continuation of work on their absorption spectra.

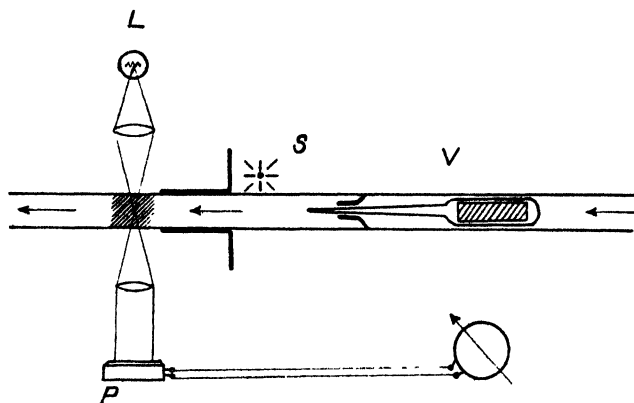


FIG. 1.—Experimental arrangement. S—spark, V—valve, L—auto lamp, P—photocell.

The main part of the set-up is shown in Fig. 1. The compound to be evaporated was contained in a side limb connected to the tube (30 cm. in length, 1 cm. of bore) shown in the

figure. The tube led into a trap immersed in liquid air. This apparatus was made of quartz. The side limb was placed in a bath at constant temperature, which for $\text{Hg}(\text{CH}_3)_2$ was kept at -50°C. , corresponding to a saturation pressure of the vapour of the order of 10^{-1} mms. A constant flow of vapour through the quartz tube was thus produced, which could be regulated within limits by a magnetically operated valve V shown in the figure. The stream of vapour was subjected to an intense illumination from a condensed spark placed close to the tube in the vicinity of the nozzle. In the shorter ultra-violet the spark is preferable to other sources.

At a distance of about 5 cms. from the illuminated place, a thin semi-transparent layer of antimony was deposited on the walls of the tube by evaporation of a small bit of the metal. This was done *in vacuo*, the compound in the side limb being kept frozen in liquid air. The temperature of the compound was then raised to -50°C. and the distillation of the vapour into the liquid air trap started. During the whole experiment

⁴ Paneth and Hofeditz, *Ber.*, 1929, **62**, 1335; 1931, **64**, 2702, 2708. Paneth and Herzfeld, *Z. Elektrochem.*, 1931, **37**, 577.

⁵ Rice, *Trans. Faraday Soc.*, 1934, **30**, 152.

⁶ Pearson, *J. Chem. Soc.*, 1934, 1718.

⁷ Norrish, *Trans. Faraday Soc.*, 1934, **30**, 107.

the pumps were kept running. When the spark was started, the tube being meanwhile screened from the light, no change in the metal deposit was noticed, but when light was admitted, however, a gradual disappearance of the metal layer was observed.

The procedure usually adopted in such experiments with free radicals^{4, 5, 6} is to note the time required to remove a metal deposit of standard thickness. Such a method is very cumbersome and does not permit continuous readings, which are desirable when the effectiveness of various wave-lengths must be found.

To make possible a quantitative determination of the rate at which the metal layer disappears, we used the simple photometric device shown in Fig. 1. Light from an auto lamp L fed by a pair of storage batteries was projected by two lenses through the metal layer on to a selenium photo-cell P connected with a galvanometer (sensitivity 10^{-7} A). The intensity of the transmitted light was adjusted so that the galvanometer deflections could be taken as proportional to it. The deflection was assumed to be a direct measure of the changing thickness of the metal deposit. The method is very simple, but very reliable.

The metal layer does not begin to disappear immediately the illumination is started, but usually some time elapses, during which the density of layer changes very slowly. Only after this induction period does the rate of change assume a constant and readily measurable magnitude.

This time lag may be due to a thin deposit of the metal invisible to the eye which has covered the wall of the tube during the distillation of the metal *in vacuo*, and which is first removed. It is also possible that an adsorbed gas layer forms on the surface of the metal and has to be removed in order that the free radicals may react with the metal.

To test the applicability of the method the first experiments were made with acetone vapour. It was shown by Norrish⁷ that ketone molecules

split up into free radicals, and this was confirmed recently by Pearson,⁸ using the method of Paneth. Instead of a mercury arc we used a spark the electrodes of which consisted of various metals and could be easily interchanged by revolving the holders. The vapour stream was illuminated at a distance of 3 cms. from the metal deposit. The acetone container was kept at $-40^{\circ}\text{C}.$, corresponding to a saturation pressure of about 6 mm. The first electrodes used were of magnesium, which gives strong lines in the region of the continuous absorption of acetone vapour. The initial deflection of the galvanometer was taken as zero.

In Fig. 2 the change in the intensity of the transmitted light is plotted against the time. It may be seen that the rate of change is fairly constant during a time interval of forty minutes. When the magnesium electrodes are replaced by iron ones, the change of the intensity remains linear but with a different slope. The experiment was made in direct continuation of that with the magnesium spark, but for better comparison of the slopes, both straight lines are drawn from the same origin. The Fe spark does not give strong lines in the range of the absorption maximum of acetone, which explains the slower disappearance of the metal in this case.

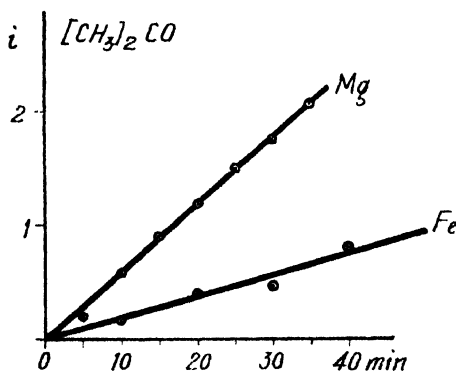


FIG. 2.—Disappearance of the metal layer with time of illumination. Mg and Fe sparks. Acetone, temp. $-40^{\circ}\text{C}.$ Distance from the layer 3 cms.

These results are substantially in agreement with those of Pearson⁸ and demonstrate the reliability of the method used.

To obtain an estimate of the life period of the methyl radicals under these conditions a metal deposit was condensed in the farther end of the tube, and the vapour stream illuminated at different distances from this place, noting each time the rate of its disappearance. The curve shown in Fig. 3 reproduces the data thus obtained. The velocity of the vapour stream and its density was not determined in this experiment and a computation of the life period is therefore postponed to another publication on the same subject.

After the preliminary experiments with acetone we turned to organo-metallic compounds. Mercury dimethyl was kept in the side limb at -50°C ., which corresponded to a saturation pressure of the order of 10^{-1} mms.

In Fig. 4 the intensity of the light transmitted by the layer of antimony is plotted as a function of the time of illumination by the sparks indicated. The rate is in general much higher than in the case of acetone and a marked difference in the effectiveness of various sparks is to be observed. From the spectral distribution of the strongest lines of these sparks⁸ a definite

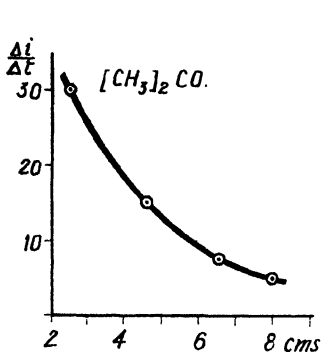


FIG. 3.—Rate of disappearance with changing distance from the layer. Mg spark.

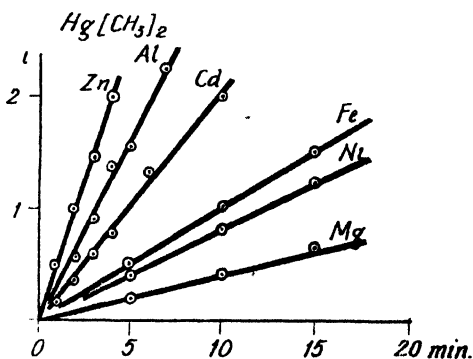


FIG. 4.—Disappearance of the metal layer with time. Illumination by various sparks. Mercury dimethyl, temp. -50°C . Distance 6 cms.

conclusion can be drawn as to the range of the active wave-lengths. The maximum sensitivity must lie between λ 2000 and λ 2150, where the strongest lines of the zinc sparks are situated. The decrease in the rate when aluminium and cadmium sparks are used, shows that wave-lengths shorter and longer than this interval are markedly less effective. The iron and the nickel sparks possess groups of strong lines in the vicinity of λ 2300 and λ 2400 respectively. The fact that all these sparks are much less effective than the zinc one is thus in agreement with the limits of the active range given above.

For a more precise determination of the active spectral range various light filters were used and the change in the rate produced by the introduction of them was noted. These light filters were: (1) a gelatin film absorbing from λ 2500 downwards, (2) a film of acetyl cellulose stained with tributyrin, absorbing from λ 2300 downwards, (3) a plate of Iceland spar absorbing from λ 2100, (4) a film of acetyl cellulose absorbing from λ 1900. By combining these filters with various sparks the relative effectiveness of different spectral ranges could be fairly well determined.

In Fig. 5 the extension of the spectral range of the active wave-lengths

⁸ Cf. for example, Terenin, *Physik. Z. Sow. Un.*, 1932, 2, 377.

is shown for mercury dimethyl. The maximum of effectiveness in producing free radicals is situated between λ 2100 and λ 2000, the long wave-length limit lying at about λ 2200. This is exactly the range occupied by the diffuse band absorption spectrum of $\text{Hg}(\text{CH}_3)_2$, described by us in a previous communication.¹ The assumption then made that the diffuseness of the spectrum was caused by a predissociation process with liberation of methyl radicals is thus confirmed.

The decrease in the effectiveness is very rapid on the long wave-length side of the maximum.

A similar series of experiments was made with $\text{Pb}(\text{C}_2\text{H}_5)_4$ vapour. The side limb containing the substance was kept at 0°C . The disappearance of the antimony layer was five to six times slower than in the case of mercury dimethyl. To obtain a measurable rate the light of the spark had to be passed along the axis of the tube. The results are summarised in Fig. 6. The experiment with different sparks and various filters could not be made with sufficient precision. We found that the maximum effectiveness is exhibited by wave-lengths situated to the longer wave-length side of the spectral range in which a strong decomposition of the vapour with the formation of a metallic dust was previously noticed.¹ This latter extends from λ 2400 towards the shorter wave-lengths. To what extent this result may be relied upon could not be decided definitely

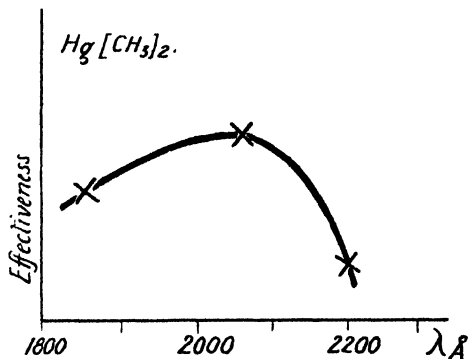


FIG. 5.—Effectiveness of various wave-lengths. Mercury dimethyl.

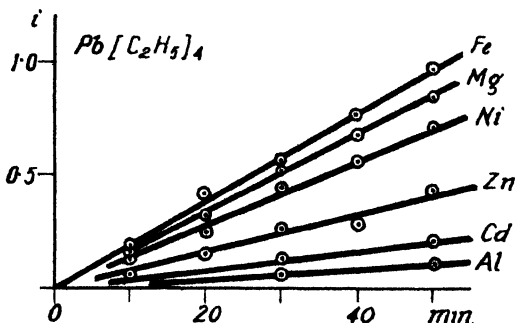


FIG. 6.—Disappearance of the metal layer with time. Tetra-ethyl lead, temp. 0°C .

owing to the small magnitude of the rate observed.

From the preliminary results described it is evident that the method is capable of further improvements and that it is well suited to a detailed study of the kinetics of free radicals in the gas phase.

Summary.

The method of detection of free alkyl radicals based on the disappearance of metal layers under their action (Paneth) was improved by measuring the thickness of the layer with the help of a photometric device with a photocell. The method was applied to the detection of alkyl radicals produced in the vapours of acetone, mercury dimethyl and tetra-ethyl lead under the action of the ultra-violet light from a spark. With the help of different electrodes and light filters the range of the most effective wave-lengths could be estimated.

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ELECTRODE DISPERSION OF NOBLE METALS.*

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1. On electrolysing an aqueous alkaline solution with a high current density, a disintegration of the material of the electrodes is often observed. According to the size of the particles, a coarse or fine suspension, or even a colloidal system, results. This phenomenon, electrode dispersion, is known with direct and alternating current. A comprehensive report on the older literature was given by Wo. Ostwald¹ in 1910. Other investigations were carried out by Lottermoser and Bausch,² Kohlschütter,³ Jirsa.⁴

2. Electrode dispersion has been observed on electrolysing a dilute solution of sulphuric acid with electrodes of noble metals, such as gold, platinum or palladium with a potential difference of, e.g., 100 volts and a high-current density. Anodic disintegration of these metals with the exception of platinum, has also been observed in most salt solutions so long as no halogen ions are present. At every potential difference a minimum concentration of the electrolyte is required. With 110 volts, this rather sharp limit appeared for gold to be 0.3 *N.* sulphuric acid and 0.2 *N.* ammonium sulphate; for platinum: 1.5 *N.* sulphuric acid, whilst no disintegration has been observed in salt solutions. At lower potential differences the concentration limits are increased.

During the dispersion, the "Wehnelt effect," a sudden fall of the strength of current to about one-tenth part, accompanied by small sparks and a peculiar crackling, as is shown by Wehnelt's electrolytical interruptor, has often been observed. Contrary to Lottermoser and Bausch's opinion, it can be demonstrated that this effect is quite independent of disintegration. It occurs without any electrode dispersion being detected, if only the temperature exceeds a certain limit, lying generally at about 50°. The concentration of the solution may be smaller than the minimum required for dispersion; thus the Wehnelt effect was, for instance, observed with normal sulphuric acid and platinum electrodes at 50° with 100 volts.

Since electrode dispersion may take place without spark-discharge, Kohlschütter's hypothesis, explaining the dispersion as the disintegration of a "disperse" oxide film by the action of the spark, cannot be correct.

The presumption that there is a connection between the electrode dispersion and pulsations of the current had to be proved by means of oscillographic methods.

3. To investigate the character of the current, a quick sixfold oscillograph constructed according to the principle of the influence of a magnetic field on an electrical conductor, was used. Fig. 1 shows an oscillogram of the current at the beginning of disintegration of a small

* Part of thesis, Amsterdam, 1935.

¹ Wo. Ostwald, *Koll. Z.*, 1910, 7, 132.

² Lottermoser and Bausch, *Z. Elektrochemie*, 1926, 32, 89.

³ Kohlschütter, *Z. Elektrochemie*, 1919, 25, 309.

⁴ Jirsa, *Koll. Z.*, 1926, 46, 28.

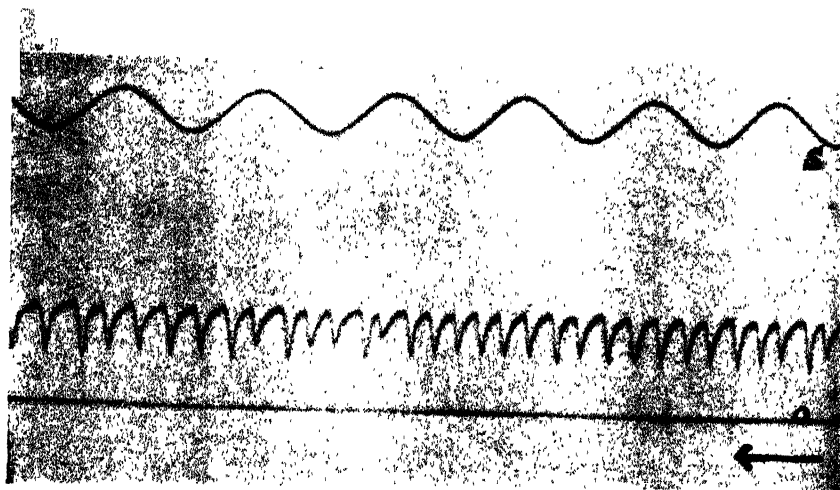


FIG. 1.

[See page 1488.]

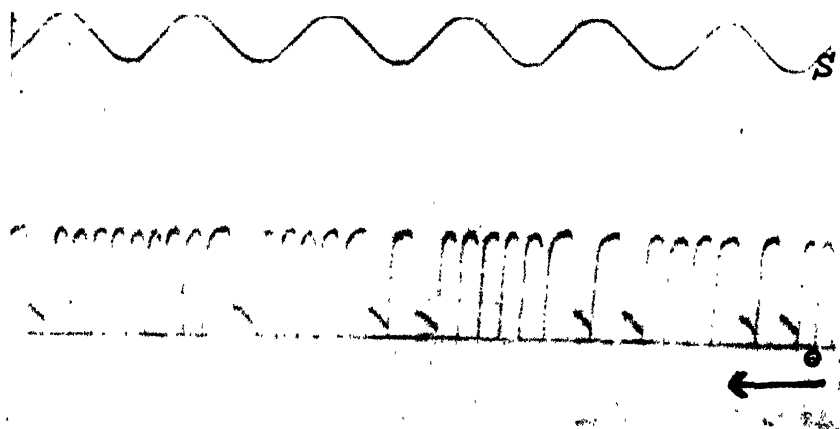


FIG. 2.

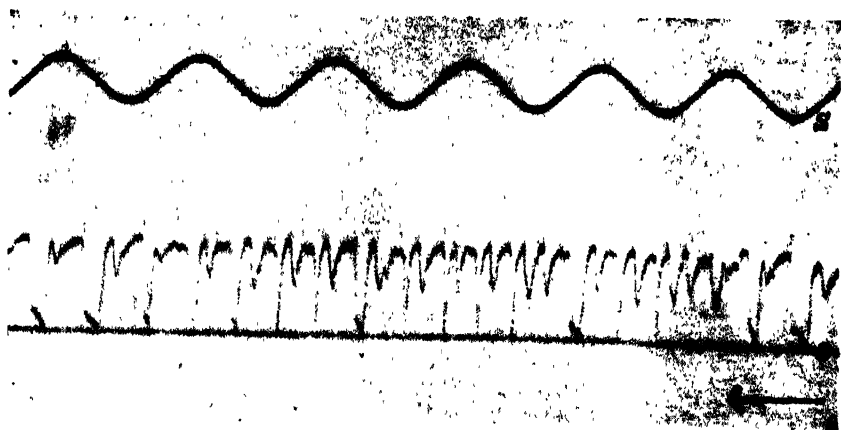


FIG. 3.

[See page 1489.]

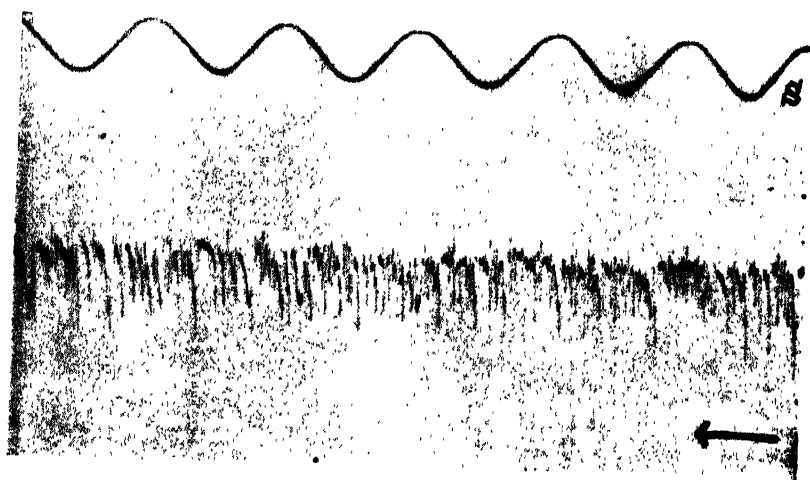


FIG. 4.

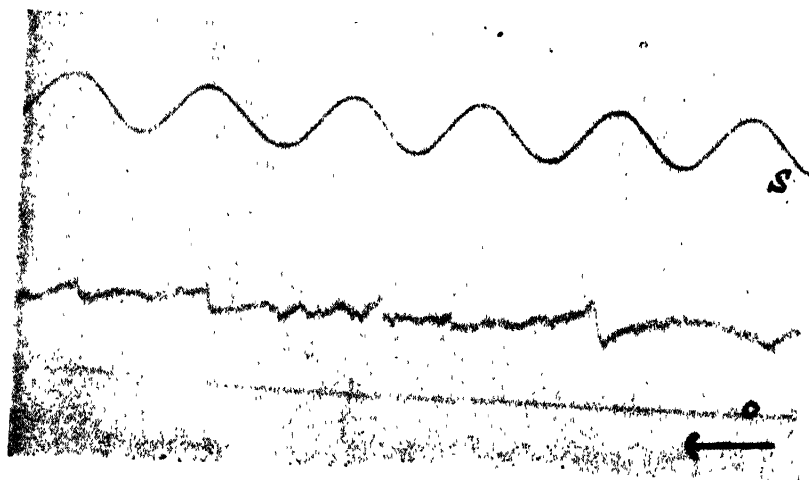


FIG. 5.

[To face page 1489.]

gold anode (area 0.3 cm.²) on electrolysing in 2 *N.* ammonium sulphate at a temperature of 30°. The potential difference, applied at the electrodes, is 110 volts, with a mean current density of 13 amp. per cm.². The curve S represents the sine curve of a 50 period alternating current, used as a time recorder while O is the line of zero strength of current.

The middle curve represents the variation in strength of current during the dispersion. A fairly regular period of approximately $\frac{1}{800}$ second is observed, while the strength of the current is decreased after every impulse to about half its value.

Fig. 2 represents an oscillogram of the same dispersion process at 40°. The mean current density is 20 amp. per cm.², and the frequency of the pulsations about 400 per second. After every impulse the current is now totally interrupted. With other concentrations, slight alterations have been found in the oscillograms. An example of the same process with a smaller concentration is given in Fig. 3.

Different metallic anodes exhibit variations in the form of the curve and the periodicity of the pulsations. The same phenomena have been observed when using solutions of different electrolytes. Pulsations with a high frequency have been observed with an electrolysis of potassium nitrate with a gold anode, the oscillogram of which shows a somewhat irregular period, the value of which, in a few cases, is less than $\frac{1}{8000}$ second (Fig. 4), while the mean value is about $\frac{1}{8000}$ second.

An oscillogram of a current during the Wehnelt effect is quite different, as is shown in Fig. 5, where slight, high frequency pulsations are visible, with a mean period of $\frac{1}{8000}$ second.

From these investigations we may conclude that every anode disintegration is accompanied by a pulsating current. Without this typical current type no dispersion whatever has been observed.

4. The alteration of the direct current to a pulsating one may be explained as a result of an anodic passivation. On the metallic surface of the anode a non-conducting film may periodically arise and be destroyed again.

This hypothesis may be further developed in accordance with the views put forward by Crowther and Stephenson.⁵ These authors explained the results, obtained in an investigation on the Wehnelt interruptor by admitting that in general almost all the resistance in the solutions is formed by a layer of oxygen which covers the anode, whilst, during the Wehnelt effect there is, in addition, a layer of superheated vapour. This layer results from the high temperature of the anode, which causes a "spheroidal state" of the liquid round the electrode.

Now it is possible to calculate the fraction of the available space on the metallic surface of the anode, which is occupied by atoms of oxygen. Considering an electrolysis during the Wehnelt effect, the number of atoms of oxygen formed is computed from the frequency of the pulsations and the strength of the current. On disintegrating a gold anode in 2 *N.* ammonium sulphate at 50° with a potential difference of 110 volts and a strength of current of 0.3 amp., a frequency of the pulsations of 3000 per second has been observed. In this case at every impulse of the current 1.0×10^{-4} coulomb are transported.

According to the reaction:



⁵ Crowther and Stephenson, *Phil. Mag.*, 1925, (6), 50, 86, 1066.

3.0×10^{14} atoms of oxygen originate from every impulse. Taking the radius of a gold atom as 1.4×10^{-8} cm., with the closest packing there will be 1.3×10^{15} gold atoms per cm.² on the surface. On the surface of the anode used, the area of which was 0.3 cm.², approximately 4.0×10^{14} gold atoms are found.

Thus at every impulse of the current about one atom of oxygen per gold atom is available, and it does not seem improbable that the cause of the interruption is to be found in the formation and destruction of a monatomic layer of oxygen round the anode.

On this view it is supposed that during the Wehnelt effect, as was found by Crowther and Stephenson, the first layer of resistance round the anode is a layer of super-heated vapour, but that the second is a monatomic layer of oxygen. As the resistance of the vapour layer is dependent upon its extent, which is connected with the temperature of the anode, it will show only slow and slight variations. This is not the case with the monatomic oxygen layer which is built up immediately after the beginning of the electrolysis. It may be suggested that this layer is broken down and destroyed by the high potential difference. A new formation of the layer immediately follows, after which the same phenomenon is repeated, and so on. As the resistance is relatively small, the successive formation and destruction of the monatomic layer causes slight pulsations with a high frequency. This is clearly shown in Fig. 5.

The mean strength of current during this dispersion was 0.3 amp. with the potential difference of 100 volts. The resistance, 330 ohm., proceeds from the layers round the anode, as the resistance in the liquid is negligible. From the variation of the height of the middle curve above the zero line it can be estimated that the conductivity of both layers together is only about 10 per cent. lower than the conductivity of the vapour layer. The resistance of this layer is therefore about 300 ohm., and that of the monatomic oxygen layer 20-30 ohm., or approximately 10 ohm. per cm.².

In a disintegration process at a lower temperature without the Wehnelt effect, the structure of the layer of resistance round the anode is different. This layer, consisting of oxygen, is formed at the beginning of the electrolysis and is gradually enlarged, causing an increase in the resistance. Afterwards the layer reaches such a thickness (according to calculations, of at least a hundred atoms) that the resistance becomes practically infinite, and the passage of the current is totally cut off. At this point the layer is broken down and destroyed by the high potential difference, after which a rise in the strength of current is at once observed. Immediately afterwards the layer is formed anew and the phenomenon is repeated *ad infinitum*.

These views lead to an explanation of the mechanism of the electrode dispersion. During the formation of the layer round the anode the "adsorbed" atoms of oxygen are subjected to forces from the metallic atoms of the anode surface. During the periodical destruction of the surface layer, the "surface oxide" remains intact, and is flung into the liquid, after which it is decomposed into a more stable oxide and the metal. The disintegration products which have been observed, are in agreement with these views. In alkaline or neutral solutions, metallic oxides and metals are found, whilst in acid solutions the oxide dissolves and a suspension of metallic particles, accompanied by metallic ions, is formed.

Summary.

1. On electrolysing with electrodes of noble metals with a high current density and a high potential difference, not only in alkaline, but also in acid and neutral solutions, a disintegration of the anode is observed from which generally unstable suspensions result.
2. Every electrode dispersion is accompanied by frequent pulsations of the current.
3. To obtain electrode disintegration, for every potential difference a minimum concentration of the electrolyte is required.
4. The Wehnelt effect is not the cause of the electrode dispersion.
5. The electrode dispersion may be explained as the result of the repulsion of a periodically formed "oxide" layer on the surface of the anode.

The author wishes to express his thanks to Professor A. H. W. Aten and to Dr. E. H. Buchner, of this University, for their kind interest and useful suggestions.

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DIAMAGNETIC STUDY OF STRUCTURE BY A NEW PLAN.

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Received 21st June, 1935.

Introduction.

Regarding the two diamagnetic standards utilised in the present paper, it should be stated that, where necessary, all Pascal's data have been corrected to the basis 0.72 for water, and that all Pauling's values and those derived therefrom have been recalculated on the basis of the physical constants (e , m , etc.) given by R. T. Birge, *Physic. Rev. Suppl.*, 1, 1, 1929.

Pascal's data have given many indications of their reliability: they fit well together into a system and in many cases have been confirmed by experimental methods entirely different from those of Pascal. Their reliability depends upon experimental accuracy.

Into the consideration of Pauling's standards, the question of reliability, in this sense, does not enter. Experiment can only check their reliability when the atoms or ions with which they are compared can be claimed to be free. This claim would be admitted for the smaller inert gases, where, however, only fair agreement is obtained; but a number of small ions have been found by the present authors to coincide in solution with the Pauling ideal to within experimental error, and thus to confirm the Pauling standards up to ions with the Argon rare gas structure. The assumptions made in setting up the standards become progressively less applicable as the atomic weight increases, but the evidence from experimental data for these

larger atoms or ions, wrongly regarded as free, makes these standards, in many instances, appear further out than they really are.

The usefulness of such a system of standards as Pauling's does not depend on confirmation of the individual values by experiment; provided the test reveals a systematic variation in the deviation between the standard and the free atom or ion, the correctness of the relations of the standards is confirmed. Such check of the individual value as is yielded by experiment provides support for the validity of the assumptions used in setting up the standards; but the use of the standards is mainly as co-ordinates of reference against which to gauge the observable and for that purpose only the relations of the individual values require to be correct. These requirements are met by the Pauling standards.

The standards which have been tested directly by the best available methods, will incidentally be put to a further test, when they come to be utilised in investigations. The researcher is very seldom called upon to deal with an atom or ion for which there is any claim that it is free. The atom or ion that has to be measured is usually a combined one, for which there must be a deviation, when comparison is made with the same atom or ion in the ideal free state. The crucial test for a set of ideal standards is that it provides a set of deviations, all in the same direction, that display systematic variation and are adaptable to interpretation. There is abundant proof that Pauling's ideal diamagnetic standards meet this requirement.

The deviation between the standard ideal free and the observed combined atom is regarded in the present paper as essentially not an error but a property inherent in the nature of the substance and as providing a valuable source of information.

For the deviation between the quantum mechanically derived ideal free atom and the observed combined atom, the variation is shown by experiment to be systematic. The interpretation of this systematic variation is suggested by a further application of quantum mechanics to the simple case of hydrogen, whereby there is provided a simple model of the sub-molecular diamagnetic details, showing how and where the depressions originate, and their order of magnitude. The quantum mechanical results obtained in this way confirm the empirical numbers obtained by the method of the present paper and provide a theoretical basis for the set of bond depressions established here.

Quantum mechanical calculation gives for hydrogen :

Pure diamagnetism of two free atoms	= 4.746 (Pauling). ¹
Pure diamagnetism of molecule	= 4.66 (Wang). ²
High frequency paramagnetism developed in bond	= 0.51 (Van Vleck). ³

Thus the observable or experimental molecular diamagnetism should be the sum of Pauling's atomic diamagnetisms minus the total depression.

The total depression is, in small part, real lowering of pure diamagnetism, and, in great part, masking (without lowering) of pure diamagnetism by the development of high-frequency paramagnetism.

The experimental values for molecular hydrogen are 3.94 (Wills and Hector) and 3.99 (Soné).⁴

Although the quantum-mechanical calculation of these depressions has hitherto been carried out only for the molecule of hydrogen, the depression observed in other molecules may be regarded as the sum of separate bond depressions each analogous to that observed in the bond of the hydrogen molecule.

¹ L. Pauling, *Proc. Roy. Soc.*, 1927, 114A, 181.

² S. R. Wang, *Phys. Rev.*, 1928, 31, 579; *Proc. Nat. Acad.*, 1927, 13, 798.

³ J. H. Van Vleck and A. Frank, *Proc. Nat. Acad.*, 1929, 15, 539.

⁴ Wills and Hector, *Physic. Rev.*, 1924, 23, 209; Hector, *Physic. Rev.*, 1924, 24, 418; T. Soné, *Phil. Mag.*, 1920, 39, 305.

For any molecule, the following relations hold between the Experimental Molecular Diamagnetism and Pascal's and Pauling's standards: *

$$\text{Expt. Mol. Dia.} = \text{Theor. Mol. Stand.} - \Sigma \text{ Bond Dep.} \quad (1)$$

$$\text{Expt. Mol. Stand.}^{\dagger} = \Sigma \text{ Pascal's atomic standards} + \text{Pascal's corrections} \quad (2)$$

$$\text{Expt. Mol. Stand.} = \text{Theor. Mol. Stand.} - \Sigma \text{ Bond Dep.} \quad (3)$$

Equation (3) holds when the substance measured has a constitution similar to those of the substances from which Pascal derived his standards and corrections, because under these conditions, $\text{Expt. Mol. Dia.} = \text{Expt. Mol. Stand.}$, and equations (1) and (3) become identical.

When all the depression of molecular diamagnetism (*i.e.* depression of $\text{Theor. Mol. Stand.}$) is regarded as seated in the bonds, then total depression = $\Sigma \text{ Bond Dep.}$ The depression of each bond is numerically equal to the sum of the bond high frequency paramagnetism and the fall of pure diamagnetism in the bond.

A. To apply equation (1), it is necessary first to decide which stage of ionisation will give the correct $\text{Theor. Mol. Stand.}$, since Pauling's inert gas structure will scarcely ever be suitable. The partition of the molecule into monatomic ions is here carried out by an improved method which follows definite regulative principles based on the dipole moments of the bonds of the known (or supposed) structure.

B. For the ions so selected, it is necessary to calculate the appropriate diamagnetisms. This is done by an extension of Pauling's method whereby Pauling's screening constants are broken up by the aid of data from optical spectra into the smaller screening constants required when the calculation has to be made for any stage of ionisation.

Thus, the $\text{Theor. Mol. Stand.}$ is calculated precisely for a known (or supposed) structure.

C. *Application of equation (1) to determine depressions of various bonds.*—By proceeding from substances of known structure and bonds all of one kind to those with bonds of two kinds, then to those with bonds of three kinds, and so on, a table of bond depressions can be built up. The measurements of Pascal and his atomic standards and corrections are so reliable that they can be used to determine the Expt. Mol. Dia. required for this application.

D. *Application of equation (1) to establish constitution.*—For any suggested structure, $\text{Theor. Mol. Stand.} - \Sigma \text{ Bond Dep.}$ can be worked out from the Tables of this paper, and if the number obtained coincides with the Expt. Mol. Dia. , then the supposed structure is supported.

As illustrations of the interpretation of diamagnetism to establish structure, the details are worked out for the cases of benzene, naphthalene, acid carboxyl group, water and hydrogen peroxide, and various features of structure, including resonance, are now quantitatively accounted for.

A. Partition of Molecule into Ions.

The theoretical atomic standards of Pauling were for free ions of the inert gas structure, and therefore in the 1S_0 state. Usually the

* The contractions used have the following meanings :

Expt. Mol. Dia.	Experimental molecular diamagnetism.
Expt. Mol. Stand.	Experimental molecular standard (Pascal).
Theor. Mol. Stand.	Theoretical molecular standard (Pauling). Sum of pure diamagnetism of free atoms or ions calculated by the Pauling method or its modification described here.
$\Sigma \text{ Bond Dep.}$	Sum of the depressions of the individual bonds, whether single or multiple.
$\Sigma \text{ Pascal's atom standards.}$	Sum of atomic standards obtained by Pascal from experimental data.

[†] P. Pascal, *L'Additivité des Propriétés Diamagnétiques*, Société de Chimie-physique (1913), or subsequent paper.

observable state of an atom is neither one of isolation nor of inert gas structure. The only observable atoms answering this description are those of the inert gases themselves. The only other observable atoms that might approach this state are monatomic non-solvated electrolytic ions of inert gas structure, which might be sufficiently free from the influence of environment to approximate diamagnetically to the Pauling isolated inert gas state. Most substances are observable only in the state of aggregates of atoms, or in the state of molecules consisting of two or more atoms. These constituent atoms are usually at stages of ionisation intermediate between the extremes where the structure is that of an inert gas. It is useful, from ideal atoms at intermediate stages of ionisation, to construct ideal molecules with which to compare diamagnetically the actual molecules, that is to compare Theor. Mol. Stand. with Expt. Mol. Dia. (see above). The need has, therefore, been felt for diamagnetisms of stages of ionisation different from those of Pauling, and intermediate stages have already been adopted by researchers.⁶ The atoms at some of these stages are paramagnetic. In the study of a diamagnetic molecule, however, this does not introduce any difficulty, since any paramagnetism present in the free atom is cancelled out when that atom becomes part of the molecule. This consideration also clears the way for the further step, to be taken now, in the process of interpolation, whereby there is obtained the diamagnetism of an atom for any stage of ionisation, without restriction as to its charge, which may be whole-numbered or fractional according to the sub-molecular structure.

In previous work where intermediate stages of ionisation were adopted, the choice of the stage was by a method of trial and error, to a certain extent. In the present paper, the most suitable stage of ionisation to be assigned to the constituent atoms of an ideal molecule is considered to be that corresponding to the residual electric charges derived from dipole moments of the actual molecule.⁷

Thus, for hydrogen chloride, let Δe = residual charge and d = distance between the nuclei. Then, the dipole moment = $\Delta e \times d$. Therefore $\Delta e = \frac{\text{moment}}{d} = \frac{1.03 \times 10^{-18}}{1.27 \times 10^{-8}} = 0.81 \times 10^{-10}$. When expressed in terms of the charge of an electron $\Delta e = \pm \frac{0.81}{4.77} = \pm 0.170$.

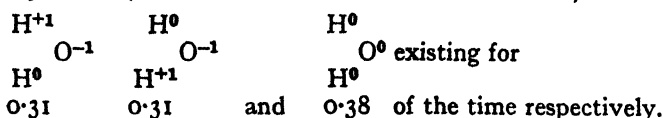
This new plan has the special merit that the selection of the charges follows definite regulative principles, and that diamagnetism is linked up with other properties. This method, in most cases, necessitates the assignment of fractional charges, which, however, are quite allowable for the statistical view of sub-molecular structure.

The significance of a fractional charge assigned to an atom, whether in the actual or the ideal molecule, is taken to be that during a portion of the time the atom has a certain whole-numbered charge, and during the rest of the time another whole-numbered charge. For example, for monomolecular water, $\text{O} \begin{array}{l} \nearrow \text{H} \\ \searrow \text{H} \end{array}$, in each hydrogen oxygen bond, H has a charge of $+0.31$ and $\text{O} - 0.31$. Thus, the molecule consists of two

⁶ Gray and Farquharson, *Phil. Mag.*, 1930, 10, 191; K. Kido, *Tôhoku Imp. Univ. Sc. Rep.*, 1933, 835.

⁷ N. V. Sidgwick, *The Covalent Link in Chemistry*, pp. 154-156, Oxford University Press, 1933.

hydrogen atoms each with a charge of $+0.31$, and one oxygen atom with a charge of -0.62 . This means that oxygen is in the forms O^{-1} and O^0 during 0.62 and 0.38 of the time respectively, whilst each hydrogen atom is in the forms H^{+1} and H^0 during 0.31 and 0.69 of the time respectively. Thus, there are three forms of the molecules,



To obtain the *theoretical molecular standard*, then, it is necessary to have first the atomic diamagnetisms for whole-numbered charges, and then to take whatever fractions of these atomic diamagnetisms are indicated by the fractional times, obtained from the dipole moments.

B. Calculation of Diamagnetism of Free Ions.

To calculate the atomic diamagnetisms for whole numbered charges the formula¹

$$-1.975 \times 10^{-6} \sum_{\kappa} \frac{n_{\kappa}^4}{(Z - S_{\kappa})^2} \left[1 - \frac{3l_{\kappa}(l_{\kappa} + 1) - 1}{5n_{\kappa}^2} \right] \quad (4)$$

was utilised, where the factor 1.975 is based on the values of the physical constants (e , m , etc.) given by R. T. Birge, *Phys. Rev. Suppl.*, 1929, **1**, 1.

and n = total quantum number,
 l = subsidiary quantum number,
 S_{κ} = screening number on electron κ .

The summation is taken over all the electrons κ .

The first requirement is the screening number on the electron κ by each other electron in the atom, in the same layer as well as in shells further in and further out. Pauling's screening number gives the resultant effect by all the screening electrons. It is necessary to split up his number and obtain separately the effect due to each screening electron. To do this, screening numbers obtained from spectral energy formulæ are considered, and by their aid the total screening on an electron is portioned out amongst the contributing electrons. Table I. shows how the necessary screening numbers required for each ion can be built up.

The formula giving the energy² associated with an electronic energy level holds strictly only for hydrogen-like ions. From it, is calculated the screening by the inner shell on one electron in an outer shell. The formula expressing doublet separation of the alkali-like ions³ is not considered to give so reliable a figure.

From triplet term separations of ions¹⁰ in the $1s^2 2p^2$ state, a screening number is obtained; from this is subtracted the screening number of the doublet for ions in the $1s^2 2p^1$ state. Although the absolute values may not be very reliable, this difference gives accurately the screening on a $2p$ electron by another $2p$. The addition of further $2p$ electrons causes the same increment in screening.

² Bacher and Goudsmit, *Atomic Energy States*, McGraw-Hill, 1932.

³ Millikan and Bowen, *Physic. Rev.*, 1924, **24**, 209.

¹⁰ Pauling and Goudsmit, *Structure of Line Spectra*, pp. 62, 101, McGraw-Hill, 1930.

TABLE I.—SCREENING NUMBERS.

	by	1s	2s	2p	$\begin{Bmatrix} 1s \\ +2s^2 \\ +2p^2 \end{Bmatrix}$			$\begin{Bmatrix} 1s^2 \\ +2s \\ +2p^2 \end{Bmatrix}$			— — —
C	1s	.228	o	o	$\begin{Bmatrix} 0.228 \\ 0.0 \\ 0.0 \\ \hline 0.228 \end{Bmatrix}$			$\begin{Bmatrix} 0.228 \\ 0.0 \\ 0.0 \\ \hline 0.228 \end{Bmatrix}$			—
	2s	.8225 a	.32 d	.216 e	$\begin{Bmatrix} 1.645 \\ 0.32 \\ 1.296 \\ \hline 3.261 \end{Bmatrix}$			$\begin{Bmatrix} 1.645 \\ 0.32 \\ 1.08 \\ \hline 3.045 \end{Bmatrix}$			—
	2p	.9625 a	.2925 c	.32 b	$\begin{Bmatrix} 1.925 \\ 0.585 \\ 1.60 \\ \hline 4.110 \end{Bmatrix}$	C-4		$\begin{Bmatrix} 1.925 \\ 0.585 \\ 1.28 \\ \hline 3.790 \end{Bmatrix}$	C-3		—
N	1s	.228	o	o	$\begin{Bmatrix} 0.228 \\ 0.0 \\ 0.0 \\ \hline 0.228 \end{Bmatrix}$			$\begin{Bmatrix} 0.228 \\ 0.0 \\ 0.0 \\ \hline 0.228 \end{Bmatrix}$			—
	2s	.8175 a	.33 d	.216 e	$\begin{Bmatrix} 1.635 \\ 0.33 \\ 1.296 \\ \hline 3.261 \end{Bmatrix}$			$\begin{Bmatrix} 1.635 \\ 0.33 \\ 1.080 \\ \hline 3.045 \end{Bmatrix}$			—
	2p	.9575 a	.2725 c	.33 b	$\begin{Bmatrix} 1.915 \\ 0.545 \\ 1.65 \\ \hline 4.110 \end{Bmatrix}$	N-3		$\begin{Bmatrix} 1.915 \\ 0.545 \\ 1.32 \\ \hline 3.780 \end{Bmatrix}$	N-2		—
O	1s	.228	o	o	$\begin{Bmatrix} 0.228 \\ 0.0 \\ 0.0 \\ \hline 0.228 \end{Bmatrix}$			$\begin{Bmatrix} 0.228 \\ 0.0 \\ 0.0 \\ \hline 0.228 \end{Bmatrix}$			—
	2s	.8125 a	.34 d	.216 e	$\begin{Bmatrix} 1.625 \\ 0.34 \\ 1.296 \\ \hline 3.261 \end{Bmatrix}$			$\begin{Bmatrix} 1.625 \\ 0.34 \\ 1.080 \\ \hline 3.045 \end{Bmatrix}$			—
	2p	.955 a	.25 c	.34 b	$\begin{Bmatrix} 1.910 \\ 0.50 \\ 1.70 \\ \hline 4.110 \end{Bmatrix}$	O-2		$\begin{Bmatrix} 1.910 \\ 0.50 \\ 1.36 \\ \hline 3.770 \end{Bmatrix}$	O-1		—

(a) From term values.

(b) From doublets and triplets, $2p^3$ triplets minus $2p$ doublet.(c) Calculated from Pauling's 4.11 and (a) and (b). (c) also supported by $2s$ $2p$ triplet minus $2p$ doublet.

(d) Assumed same as (b) for same atom.

(e) Calculated from Pauling's 3.26 and (a) and (d).

The screening by $2s$ on $2p$ is found by difference.* Thus, the screening number given by Pauling for L_{II} L_{III} levels can be completely broken up. For the L_I level, it is assumed that $2s$ screens $2s$ by the same amount as $2p$ screens $2p$, and the screening by $2p$ on $2s$ is estimated by difference.

These figures show, as would be expected, that as the nuclear charge increases, the larger outer orbits contract more than the inner orbits; thus, with increasing Z , $1s$ screens both $2s$ and $2p$ less efficiently; $2s$ screens $2p$ less. On the other hand, the electrons in the same level are brought into closer relationship, and their increased mutual action leads to an increase in screening number; thus, the screening by $2p$ on $2p$ increases. The two opposite effects are seen balanced in the screening by $2p$ on $2s$. In an ion of the inert gas structure, where all the shells are complete, these effects so balance that the total screening number for any level is independent of Z .

The atomic diamagnetism for various stages of ionisation for whole-numbered charges is given in Table II., and the residual charges for various bonds are shown in Table III.

With the figures in these tables it is now possible to compute the theoretical molecular standard. (Theor. Mol. Stand.)

TABLE II.—IONIC DIAMAGNETISMS.

H ⁰ 2.373	C ⁺⁴ 0.15	N ⁺⁵ 0.11	O ⁺⁶ 0.08
H ⁻¹ 7.954	C ⁺³ 1.90	N ⁺⁴ 1.21	O ⁺⁵ 0.86
	C ⁺² 4.23	N ⁺³ 2.72	O ⁺⁴ 1.90
	C ⁺¹ 6.64	N ⁺² 4.12	O ⁺³ 2.74
	C ⁰ 9.96	N ⁺¹ 5.91	O ⁺² 3.91
	C ⁻¹ 14.69	N ⁰ 8.28	O ⁺¹ 5.32
	C ⁻² 21.56	N ⁻¹ 11.45	O ⁰ 7.09
	C ⁻³ 32.00	N ⁻² 15.76	O ⁻¹ 9.40
	C ⁻⁴ 48.78	N ⁻³ 21.89	O ⁻² 12.66

TABLE III.†—RESIDUAL CHARGES DUE TO UNEQUAL SHARING OF BOND ELECTRONS.‡

+ -	+ -	+ -	+ -
H-C 0.04	H-N 0.29	C-Cl 0.21	H-F 0.46
H-O 0.31	H-S 0.13	C-Br 0.17	H-Cl 0.170
C-O 0.13	C-N 0.06	C-I 0.15	H-Br 0.116
C=O 0.42	C=N 0.25		H-I 0.050
C-S 0.15	C≡N 0.61		
C=S 0.40	N-O 0.08		
	N=O 0.34		

* For confirmation of the result see reference 10, page 102.

† Values for N→O and N=O are from unpublished measurements carried out in this department by Cruickshank.

It is to be noted that the depression for any co-ordinate bond is usually about a fourth of the corresponding co-valent bond.

The value for O→H was obtained from water on the assumption that there is perfect co-ordination in liquid water at ordinary temperature. If we regard perfect co-ordination as being reached only in ice, then the value for molecular diamagnetism in liquid water for perfect co-ordination would be a little greater than 12.96 and a value for O→H a little less than 0.215 would be obtained, say about 0.15, which is nearer a fourth of 0.67.

C. Setting up a Table of Standard Bond Depressions.

The theoretical molecular standard (Theor. Mol. Stand.) is calculated by adding together the diamagnetisms of free ions as given in Table II., taking such fractions of those diamagnetisms as are indicated by the fractional times obtained from the dipole moments.

Always, Theor. Mol. Stand. is greater than Expt. Mol. Dia. as indicated by equation (1), the drop being due to bond formation.

This difference between two numbers (one obtained by calculation and the other by measurement) is the most important quantity in diamagnetic research. Its interpretation yields most valuable clues to sub-molecular structure.

Long before the advent of quantum mechanics made possible the calculation of the diamagnetism of the free ions by the Pauling method, Pascal published his experimental atomic standards for which equation (2) holds. His corrections were made for double and triple bonds and other special features of structure. His atomic standards were obtained from simple structures for which there are no Pascal corrections.

Expt. Mol. Dia. = Expt. Mol. Stand. when the substance measured has a constitution similar to those of the substances from which Pascal derived his standards, and only when this is the case does Expt. Mol. Stand. equal Theor. Mol. Stand. minus Σ Bond Dep. (equation 3).

Agreement between Theor. Mol. Stand. and Expt. Mol. Dia. always involves a *want of coincidence* (except for the inert gases), Expt. Mol. Dia. being less than Theor. Mol. Stand.

Agreement between Expt. Mol. Stand. and Expt. Mol. Dia. involves *either coincidence or deviation*, Expt. Mol. Dia. being equal to, greater than or less than Expt. Mol. Stand.

The relation between these two sets of standards is shown in equation (3) (when Expt. Mol. Stand. = Expt. Mol. Dia.).

Pascal's measurements and his atomic standards and corrections are so reliable that they can be used in equation (3) to determine the Bond depressions. In this connection, it may be pointed out that for the CH_3 group, eight values (average 11.87), very close to Pascal's 11.86, have been obtained recently in this Department from three different homologous series, organic nitrites, nitrates and nitro-compounds, by measurements with a Curie-Chéneveau balance. This confirmation of Pascal's value is the more important because he used non-torsional methods. On the other hand, Bhatnagar is at present undertaking a critical experimental study of Pascal's standards by an interferometer method, and in a recent paper¹¹ adopted revised figures (average 11.355) for the CH_3 group. However, the obtaining of the value 11.87, quoted above, has so strengthened reliance on Pascal's data, and his figures have generally been found so reliable, that the present researchers have every confidence in retaining Pascal's value in preference to Bhatnagar's. In support of the latter value much more evidence requires to be forthcoming before a place can be claimed for it as a rival to the firmly established Pascal value.

By proceeding from substances of known structure and bonds all of one kind, to those with bonds of two kinds, then to those with bonds of three kinds, and so on, a table of bond-depressions can be built up.

The depression due to each bond is calculated by considering the series of simple molecules from which the Pascal standards were originally

¹¹ S. S. Bhatnagar, N. G. Mitra, and G. D. Tuli, *Phil. Mag.*, 1934, 18, 449-456.

computed. How this depression is computed, and the extent to which it varies with the nature of the bond, will be understood from the actual examples given.

The Carbon Carbon Single Bond in Diamond.

Each carbon is linked to four other carbon atoms. The experimental diamagnetism of diamond per carbon atom, therefore, includes four half-bonds or two whole bonds. When two like atoms participate in a bond there is no dipole moment. Each atom is to be taken as neutral.

Thus the diamagnetisms are :

Theoretical free neutral C atom	. . .	9.96
In diamond : C + 2 bonds	. . .	6.0
		<hr/>
Depression per two bonds	. . .	3.96
Depression per carbon carbon single bond	. . .	1.98

The Carbon Hydrogen Bond in the CH₃ Group.

By comparing the members of a homologous series, Pascal obtained for the diamagnetism of this group the value 11.86. This value includes two whole carbon-hydrogen bonds and two half carbon-carbon single bonds, or, instead of the two halves, one whole carbon-carbon single bond (see Fig. 1). In each carbon-hydrogen bond there is unequal sharing of the electrons, the dipole moment indicating a charge of +.04 for H and -.04 for C, or in the CH₃ group the charges are -.08 for C and +.04 for each H. This means that C is in the forms C⁻¹ and C⁰ for .08 and .92 of the time respectively, and each H is in the forms H⁺¹ and H⁰ for .04 and .96 of the time respectively.

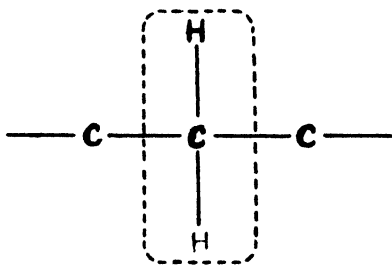


FIG. 1.

Thus the computed diamagnetisms are :

For C	{	.08 × 14.69 = 1.18	
	{	.92 × 9.96 = 9.16	
For 2H	{	2 × .04 × 0 = 0.0	
	{	2 × .96 × 2.373 = 4.56	
		<hr/>	14.90
Experimental diamagnetism	. . .		11.86
		<hr/>	
Depression	. . .		3.04
Depression for one carbon carbon single bond	. . .		1.98
		<hr/>	
Depression for two carbon hydrogen bonds	. . .		1.06
Depression per carbon hydrogen bond	. . .		0.53

The assumption that the C—C bond depression is the same in hydrocarbons as in diamond is, of course, not strictly correct, but experience has shown it to be near enough to the truth to be justifiable.

By similar methods applied to simple types of substances, the depression for a number of bonds are obtained. In Table IV are collected

TABLE IV.*—BOND DEPRESSIONS OF DIAMAGNETISM.

Co-ordinate Bonds.	Single Bonds.	Double Bonds.	Triple Bonds.
O→H 0.215 water C→C 0.43 benzene	C—H 0.53 CH ₄ N—H 0.57 CH ₃ NH ₃ O—H 0.67 CH ₃ OH C—C 1.98 diamond C—N 1.78 (CH ₃) ₃ N C—O 1.92 (CH ₃) ₂ O N—O 2.06 NH ₂ OH H—H 0.596 in H ₂ mol. calc. by quant. mech.	C=C 9.50 ethylene C=N 11.77 Pascal † C=O 10.28 acetone N=O 13.90 alkyl nitrite	C≡C 6.73 acetylene C≡N 5.50 methyl nitrile
C→O 0.42 by analogy from C—C N→O 0.52 from solutions of nitrates O→O 0.60 estimated			

these depressions and the substances from which they have been derived. To the substances has been applied the equation: Expt. Mol. Stand. = Theor. Mol. Stand. — Σ Bond Dep. (3), Pascal's Expt. Mol. Stand. giving accurately the Expt. Mol. Dia.

Because equation (3) is so widely applicable, it is clear that the molecular diamagnetism will, in many cases, have the same value whether calculated from Theor. Mol. Stand. and Bond Depressions, or, from Pascal's atomic standards and his corrections.

When Pascal builds up the molecular diamagnetism, he in some cases does not mention depression at all, as in the simple substances containing only single bonds, and in other cases he portions out the depression wrongly among the atoms. For example, Pascal's experimental atomic standard for carbon is 6 (from diamond), and therefore has already been subjected to the depression which the free carbon atom undergoes when it enters into union by single bonds with other carbon atoms. Pascal does not direct attention to this depression, but finds that a depression, 5.55, has to be corrected for when carbon enters into union by double bonds. This depression, 5.55, is in addition to the depression carbon has already undergone when it combines by single bonds.

In the present system the depression for the double carbon carbon bond is 9.50. This agrees with the number obtained by adding together the depressions for two single carbon carbon bonds 3.96, and Pascal's correction 5.55. This seems to give the wrong impression that a double bond is made up of two single bonds which are then modified in some way. Similarly, in all other cases, Pascal's corrections are in addition to the depression which is inherent in his atomic standards and which is due to single bonds. Pascal's analysis is therefore artificial in its special treatment of single bonds.

Further, his method is faulty in its wrong portioning out of the depressions to the different atoms. For example, from the values for diamond and CH₄, Pascal obtains his standards C = 6 and H = 2.93. From the Theor. Mol. Stand., 14.90, for the group, the Expt. Mol. Dia. shows a depression of 3.04 which seems to be wrongly portioned out by Pascal among the three atoms. More correct depressions would appear to be 2.51 in C and .53 in the two hydrogens, or 0.265 per hydrogen, and

* See footnote †, p. 1497.

more correct assignment of atomic values are for C 7.84 instead of 6 and for H 2.01 instead of 2.93. The value 2.01 for H was computed on the assumption that H and C share equally in the loss sustained in the CH bond, whilst probably C loses rather more than H, and the value for H is rather greater than 2.01.

Among Pascal's atomic standards H is the only atom showing a rise above the theoretical neutral value. It is here represented as normal, that is, as displaying a depression below 2.373. This assignment of a lower value to H is supported by other experimental evidence.

Thus Pascal's atomic standards should vary even when only single bonds are considered, as is seen for C (6 in diamond and 7.84 in CH_4). This holds still more clearly for more complex structures, where Pascal's corrections really imply assigning variable values to the atoms. Pascal recognises the variability of oxygen, but all the atoms should share the depressions and therefore are variable both in simple and in complex substances.

D. Applications.

The system of bond depressions calculated above allows of quantitative interpretation of the diamagnetic susceptibility of many substances in terms of their constitution. For most of simple substances for which the Pascal standards hold, the molecular diamagnetism is readily interpreted in agreement with the constitution already established on chemical grounds. The empirical standards of Pascal are replaced by a system which permits of direct determination of constitution on the basis of the magnetic measurement only, and results in a pattern for the molecule reflecting in every detail the pattern of the sub-molecular structure in harmony with quantum mechanical predictions of diamagnetism and paramagnetism within the molecule. The Pascal standards, representing the older method of applying magnetic results, allowed the diamagnetic susceptibility of a substance to be used to determine its constitution by comparison with other substances of known constitution; the newer method developed here allows the experimental molecular diamagnetism to determine constitution directly, and thus to ascribe a definite constitution to those substances which the older method could only determine to be different from the substances with which they were compared.

This application, and the light thus thrown on the chemical constitution, is illustrated in the examples considered below.

Benzene.

For the benzene ring structure, Pascal gives a correction to be *added* to the sum of the atomic standards, although the usual formula contains double bonds for which his rule is to *subtract* from the additive value. The older method of interpretation only leads to the conclusion that the normal Kekulé structure for benzene is incorrect, and suggests no alternative. The newer method of this paper allows different suggested structures to be quantitatively tested by comparing the calculated molecular diamagnetism for each structure with the experimental susceptibility of benzene. It is found that the experimental figure agrees, not with one structure, but with two, each of which represents the true structure for half the time.

The two states are represented in the diagrams, and for each the

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molecular susceptibility is calculated. It is to be noted that each state exists in two alternative, but exactly equivalent, states of identical diamagnetism.

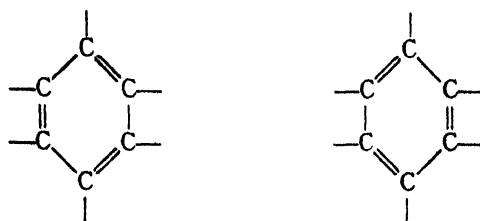


FIG. 2a.—Kekulé State.

No. of Atoms.	Charge on Each.	Diamagnetism of Each.	Total Diamagnetism.	Bond Depressions.
6 C atoms	-0.04	$\begin{cases} C^{-1} & 0.04 \times 14.69 = 0.5876 \\ C^0 & 0.96 \times 9.96 = 9.5616 \end{cases}$	$\begin{matrix} 3.5256 \\ 57.3696 \\ 13.6686 \\ 0.0 \end{matrix}$	$\begin{matrix} 6 \text{ C-H} : 3.18 \\ 3 \text{ C-C} : 5.94 \\ 3 \text{ C=C} : 28.50 \\ \hline 37.62 \end{matrix}$
6 H atoms	+0.04	$\begin{cases} H^0 & 0.96 \times 2.373 = 2.2781 \\ H^{+1} & 0.04 \times 0 = 0.0 \end{cases}$	$\begin{matrix} 74.5638 \\ 37.62 \\ \hline 36.94 \end{matrix}$	
		Theor. Mol. Stand. :		
		Bond Dep. :		
		Resultant Mol. Dia. :		

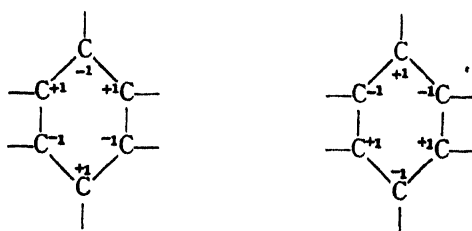


FIG. 2b.—Internal-Ionic State.

No. of Atoms.	Charge on Each.	Diamagnetism of Each.	Total Diamagnetism.	Bond Depressions.
3 C atoms	-1.04	$\begin{cases} C^{-2} & 0.04 \times 21.56 = 0.8624 \\ C^{-1} & 0.96 \times 14.69 = 14.1024 \end{cases}$	$\begin{matrix} 2.5872 \\ 42.3072 \end{matrix}$	$\begin{matrix} 6 \text{ C-H} : 3.18 \\ 6 \text{ C} \rightarrow \text{C} : 2.58 \\ \text{polar} \end{matrix}$
3 C atoms	+0.96	$\begin{cases} C^0 & 0.04 \times 9.96 = 0.3984 \\ C^{+1} & 0.96 \times 6.64 = 6.3744 \end{cases}$	$\begin{matrix} 1.1952 \\ 19.1232 \end{matrix}$	$\begin{matrix} 5.76 \\ \hline \end{matrix}$
6 H atoms	+0.04	$\begin{cases} H^0 & 0.96 \times 2.373 = 2.2781 \\ H^{+1} & 0.04 \times 0 = 0.0 \end{cases}$	$\begin{matrix} 13.6686 \\ 0.0 \end{matrix}$	
		Theor. Mol. Stand. :		
		Bond Dep. :		
		Resultant Mol. Dia. :		

When each of these structures represents the true structure for half the time, the calculated Mol. Dia. for this structure is the mean of those above.

Therefore	Calculated Mol. Dia. : $\frac{1}{2}(36.94 + 73.12) = 55.03$
	Experimental Mol. Dia. : 55.03

In the above calculations, the Theor. Mol. Stand. has to be corrected for the bond depressions. In the Kekulé state all the bond depressions are known from other simple molecules. In the internal-ionic state there are 6 C—C bonds, each of which is different from ordinary single bonds, being of a co-ordinate or polar nature because the C atoms are alternately + and —. Such bonds are known from other instances to give small depressions (see Gray and Farquharson).⁶ Assuming for the depression in this bond the value 0.43, which seems of the right order of magnitude, the experimental mol. dia. then indicates that the true structure of benzene is made up of these two states, each existing for exactly half the time.

Some properties of benzene can be described by the double-bond structure, others of its properties by the internal-ionic; its diamagnetism requires both. Since the required structures are in the very simple relationship of the same time for each, and, further, these structures describe well-known properties of benzene, their selection to interpret the diamagnetism can scarcely be described as arbitrary, especially when the only alternatives would involve structures less well known and having more complicated relationships.

Resonance has for some time been regarded as a necessary feature of benzene. The double-bond or Kekulé structure exists in two possible equivalent forms, in resonance with one another. The internal-ionic also exists in two equivalent forms in resonance. The diamagnetism requires that these four states all exist for equal times, and suggests that they all share equally in the resonance within the molecule.

Naphthalene.

The experimental molecular diamagnetism of naphthalene can be accounted for by two or more structures, in various proportions. But there seems no good reason for adopting more complicated systems, when a single structure is ready to hand which coincides exactly with diamagnetic experiment. This structure consists of two rings of which one is all the time internal-ionic and the other all the time double-bonded, as shown in Fig. 3a.

But exactly the same diamagnetism is displayed by the form of the molecule shown in Fig. 3b obtained by interchanging the ring structures of Fig. 3a. This is a clear case of degeneracy, in which the two forms are to be regarded as in resonance. The degeneracy here requires the same time for each form of the molecule; the diamagnetism requires only that one ring be internal-ionic, and simultaneously the other ring be double-bonded; it is the degeneracy that points to an interchange of the ring structures.

The rule of equal times holds for the whole molecule; it therefore must hold for each ring, which exists half the time in the internal-ionic form and half the time in the double-bonded form. Thus, there is seen within each ring resonance between two forms which are not equivalent and not diamagnetically equal.

The equality of the periods required here within each ring is analogous to the diamagnetically indicated equality of periods within the benzene ring for the internal-ionic and the double-bonded forms. It, therefore, supports this result for benzene, although the double-bonded forms are

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not quite the same for the benzene and naphthalene rings. The equal time result for benzene is, therefore, not merely due to a fortuitous coincidence of numerical values.

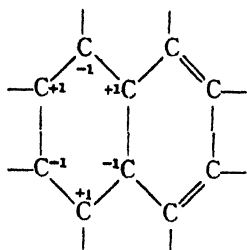


FIG. 3a. Naphthalene Structure.

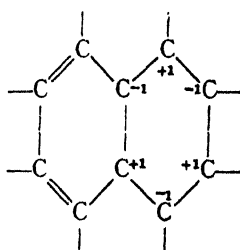


FIG. 3b.

No. of Atoms.	Charge on Each.	Diamagnetism of Each.	Total Diamagnetism.	Bond Depressions.
2 C	-1.04	$\begin{cases} \text{C}^{-1} & 0.04 \times 21.56 = 0.8624 \\ \text{C}^{-1} & 0.96 \times 14.69 = 14.1024 \end{cases}$	$\begin{cases} 1.7248 \\ 28.2048 \end{cases}$	8 C-H 4.24
2 C	+0.96	$\begin{cases} \text{C}^{+1} & 0.96 \times 6.64 = 6.3744 \\ \text{C}^0 & 0.04 \times 9.96 = 0.3984 \end{cases}$	$\begin{cases} 12.7488 \\ 0.7968 \end{cases}$	2 C=C 19.00
1 C	-1	C ⁻¹ 14.6900	14.6900	3 C-C 5.94
1 C	+1	C ⁺¹ 6.6400	6.6400	6 C→C 2.58
4 C	-0.04	$\begin{cases} \text{C}^{-1} & 0.04 \times 14.69 = 0.5876 \\ \text{C}^0 & 0.96 \times 9.96 = 9.5616 \end{cases}$	$\begin{cases} 2.3504 \\ 38.2464 \end{cases}$	polar 31.76
8 H	+0.04	H ⁰ 0.96 × 2.373 = 2.2781	18.2248	—
		Theor. Mol. Stand. Bond Dep. :	123.6268	—
			31.76	—
		Resultant Mol Dia.	91.87	—
		Experimental Mol Dia	91.54	—

It is to be noted that all the bond depressions are known in this case from other molecules.

Acid Carboxyl Group.

The Pascal Standard for this group agains corresponds with no single structure. The present method suggests that resonance is a feature of the constitution and takes place between the alternative structures :

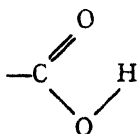


FIG. 4a.—Double-bonded.

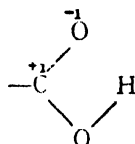


FIG. 4b.—Internal-ionic.

each state existing for exactly half the time. The value of the depression in the $\overset{+}{\text{C}}-\overset{-}{\text{O}}$ polar bond has been assumed on the analogy of the C—C and $\overset{+}{\text{C}}-\overset{-}{\text{C}}$ bonds. For acetic acid, the numerical values are :

	Double-Bonded.	Internal-Ionic.
Mol. Dia. . . .	26.86	36.36
Mean		31.61
Expt. Mol. Dia. . .		31.67

On other grounds, it is known that the two oxygen atoms are equivalent, and therefore the resonance must include an interchange of the H atom between the two oxygens. The diamagnetism of the other two structures, produced by this interchange, is the same as of the two above, and the acid carboxyl group, like benzene, is therefore compounded of four separate structures sharing equally in the resonance.

Experiment also indicates that the same structure must hold in the esters of these acids, and the alkyl group plays the same part as the hydrogen does in acids in interchanging between the O atoms.

O-Alkyl Ureas.

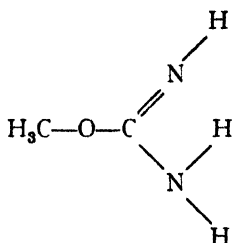


FIG. 5a.—Double-bonded.

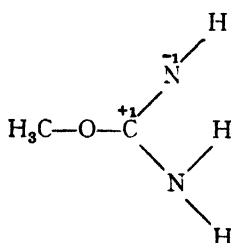


FIG. 5b.—Internal-ionic.

The magnetic susceptibility for the O-methyl and O-ethyl ureas found by Devoto (*Rend. Atti. Naz. Acad. Lincei*, 1932, **15**, 973) corresponds to the existence of similar alternative structures to those of the carboxylic acids. The structure of these urea derivatives is therefore, as in the acid group, compounded of four separate structures sharing equally in the resonance and involving the transfer of a H atom between the two equivalent N atoms.

These apparent anomalies in the Pascal system of standards are therefore capable of simple interpretation in terms of resonant structures within the molecule. The diamagnetic figures in all these cases require that in addition to the resonance occurring between two equivalent double-bonded structures, there should exist an exactly equal-timed resonance between two internal-ionic structures formed by the double bond changing to a bond of a polar nature. The double bond does not suffer this change in every case, but substances considered here seem to show that this change is a necessary corollary to the resonance in which the double bond participates by changing its position in the molecule.

The Significance of Pascal's Rule for Double and Triple Bonds.

For a double bond, Pascal gives a considerable correction to be subtracted from the additive molecular diamagnetism, whereas for the triple bond there is very little change. The correction for multiple bonds cannot, therefore, be due merely to localisation of bonds, as the effect of a triple bond would then be greater than that of a double.

A simple explanation of the multiple bond rules is obtained as follows :

It is not unlikely that a multiple bond is unable to retain all its electrons for the whole time, and that it does exist for a short time in the single state. The removal of electrons required to change from the multiple condition is probably symmetrical, that is, an equal number becomes attached to each carbon atom. The essential difference between the double and the triple bond is that the symmetrical removal of bond

are the two hydrogen atoms, and two lone pairs of electrons. In perfect co-ordination, each lone pair is co-ordinated to the hydrogen of another molecule.

By the present method, the molecular diamagnetism of water may be calculated for various stages of co-ordination, account being taken of the unequal sharing of the bonds (see Table V.).

TABLE V.—CALCULATIONS FOR WATER.

Stages of Co-ordination.	Charges.	Total Diamagnetism.	Bond Depressions.
Each O with two co-ordinate links and two co-valent links. Perfect co-ordination.	Each O + 0.76	$\{0.76 \quad O^{-1} = 0.76 \times 5.32 = 4.0432$	2 covalent = $2 \times .67 = 1.34$
		$\{0.24 \quad O^0 = 0.24 \times 7.09 = 1.7016$	O—H
	Each H - 0.38	$\{2 \times .38 \quad H^{-1} = 0.76 \times 7.954 = 6.0450$	2 co-ord. = $2 \times .215 = 0.43$
		$\{2 \times .62 \quad H^0 = 1.24 \times 2.373 = 2.9425$	O→H
		Theor. Mol. Stand. = 14.7323 Bond depressions = 1.77	1.77
Each O with one co-ordinate link and two co-valent links. Molecules forming rings.	Each O + 0.07	$\{0.07 \quad O^{-1} = 0.07 \times 5.32 = 0.3724$	2 O—H = $2 \times .67 = 1.34$
		$\{0.93 \quad O^0 = 0.93 \times 7.09 = 6.5937$	coval.
	One H + 0.31	$\{0.31 \quad H^{-1} = 0.31 \times 0 = 0.0$	1 O→H — — = .215
		$\{0.69 \quad H^0\} = 1.31 \times 2.373 = 3.1086$	co-ord.
	One H - 0.38	$\{0.62 \quad H^0\} = 1.31 \times 2.373 = 3.1086$ $\{0.38 \quad H^{-1} = 0.38 \times 7.954 = 3.0225$ Theor. Mol. Stand. = 13.0972 Bond depressions = 1.55	1.55
Each O with two co-valent links. No co-ordination.	Each O - 0.62	$\{0.62 \quad O^{-1} = 0.62 \times 9.40 = 5.8280$	2 O—H = 1.34
		$\{0.38 \quad O^0 = 0.38 \times 7.09 = 2.6942$	coval
	Each H + 0.31	$\{2 \times .31 \quad H^{-1} = 2 \times 0 = 0.0$	
		$\{2 \times .69 \quad H^0 = 1.38 \times 2.373 = 3.2747$	
		Theor. Mol. Stand. = 11.7969 Bond depressions = 1.34	
		Resultant Molecular Diamag. 10.46	

The value 10.46 for unco-ordinated or monomolecular water agrees with the sum of Pascal's atomic standards, 4.6 for hydroxylic oxygen and twice 2.93 for hydrogen. This may be expected, as Pascal's standards involve implicitly the bond depressions.

On the other hand, Pascal's figures by themselves afford no explanation of the value 12.96 for ordinary water. The uncorrected molecular diamagnetism for completely co-ordinated water, 14.73 has to be corrected for the bond depressions. Only the value for the two co-valency bonds is known; 1.34. If water is regarded as completely co-ordinated at ordinary temperature, there remains a depression of .43 to be accounted for by the two co-ordinate bonds. A very low depression is displayed by other co-ordinate bonds also. As the depression for the co-valency links O—H is only 0.67, the value 0.215 is about the right order of magnitude for the depression in the co-ordinate links O→H.

The diamagnetism of water is usually regarded as constant at constant temperature. It is clear from the above that the diamagnetism varies with the degree of co-ordination. Thus, wherever there is any factor that may affect co-ordination, it is important to take this variation into account. This question will be discussed more fully in a future communication.

The mechanism used here to explain co-ordination is the usual one in which each co-ordinated hydrogen atom has four shared electrons. Sidgwick¹² has suggested the adoption of a mechanism of resonance to avoid the assignment of four electrons to hydrogen. The structures between which this resonance occurs are limited by the requirements of the experimental molecular diamagnetism. Any resonance merely involving transfer of a H atom between neighbouring molecules results in equivalent resonant states which do not alter the diamagnetism from the value for the single molecule HOH, 10.46. Similarly, structures such as $H^{+1}(OH)^{-1}$ and $H^{+1}O^{-2}H^{+1}$ give too small a diamagnetism. Only when resonance occurs between the two equivalent structures $H^{-1}(OH)^{+1}$ and $(HO)^{+1}H^{-1}$ is it possible to obtain a calculated molecular diamagnetism greater than the experimental. The calculated value 14.79 is not in very good agreement with experiment and the diamagnetism of water favours very strongly the co-ordination structure described above, though it involves four shared electrons for each H atom.

Alcohol.

To explain the properties of hydroxylic substances like the alcohols, it has been generally assumed that a co-ordination similar to that in water is present. The magnetic values clearly show that the co-ordination in water is of a different type from that in alcohol; in water the Theor. Mol. Stand. is practically equal to the Expt. Mol. Dia.; in alcohols the Theor. Mol. Stand. is greater than the Expt. Mol. Dia. by an amount which is satisfactorily accounted for by normal bond depression. It is possible, in the case of alcohol, to explain the magnetic values by assuming, as Sidgwick does, that the so-called "co-ordination" is really a resonance involving the transfer of a hydrogen atom from one molecule to another.

This type of resonance takes place between two exactly equivalent structures, and the state of electronic distribution and therefore the distribution of magnetism in the molecule is still represented by the simple formula $R-O-H$.

Hydrogen Peroxide.

The method of the present paper has been applied to decide between the two structures most commonly suggested for hydrogen peroxide (Tables VI. and VII.).

The difference 1.02 may be accounted for partly by the depression due to the normal form of polymerisation which is present in hydrogen peroxide, and partly by the depression due to the co-ordinate link $O \rightarrow O$. The values which it is necessary to assign to these depressions need not differ much from the right order of magnitude: for example 0.6 for the $O \rightarrow O$ bond leaving 0.42 or 2.5 per cent. for the polymerisation.

¹² N. V. Sidgwick, *Ann. Rep. Chem. Soc.*, 1934, **31**, 40-43.

TABLE VI.

Structure.	Charge.	Diamagnetism.
$\begin{array}{c} \text{aH} \quad \text{c} \quad \text{d} \\ \diagup \quad \diagdown \\ \text{O} \rightarrow \text{O} \\ \diagdown \quad \diagup \\ \text{bH} \end{array}$	$\text{aH} + 0.31$	$\begin{cases} 0.31 \text{ H}^{+1} = 0.31 \times 0 = 0 \\ 0.69 \text{ H}^0 = 0.69 \times 2.373 = 1.6374 \\ 0.31 \text{ H}^{+1} = 0.31 \times 0 = 0 \\ 0.69 \text{ H}^0 = 0.69 \times 2.373 = 1.6374 \\ 0.38 \text{ O}^{+1} = 0.38 \times 5.32 = 2.0216 \\ 0.62 \text{ O}^0 = 0.62 \times 7.09 = 4.3958 \\ \text{O}^{-1} = 9.40 = 9.4000 \end{cases}$
	$\text{bH} + 0.31$	
	$\text{cO} + 0.38$	
	$\text{dO} - 1.0$	
		Theor. Mol. Stand. 19.0922
		Depression for 2 H—O bonds 1.34
		17.75
		Experimental Molecular 16.73
		Difference 1.02

TABLE VII.

Structure.	Charge.	Diamagnetism.
$\begin{array}{c} \text{H}-\text{O}-\text{O}-\text{H} \\ \text{a} \quad \text{c} \quad \text{d} \quad \text{b} \end{array}$	$\text{aH} + 0.31$	$\begin{cases} 0.31 \text{ H}^{+1} = 0.31 \times 0 = 0 \\ 0.69 \text{ H}^0 = 0.69 \times 2.373 = 1.6374 \\ 0.31 \text{ H}^{+1} = 0.31 \times 0 = 0 \\ 0.69 \text{ H}^0 = 0.69 \times 2.373 = 1.6374 \\ 0.31 \text{ O}^{-1} = 0.31 \times 9.40 = 2.9140 \\ 0.69 \text{ O}^0 = 0.69 \times 7.09 = 4.8921 \\ 0.31 \times \text{O}^{-1} = 0.31 \times 9.40 = 2.9140 \\ 0.69 \times \text{O}^0 = 0.69 \times 7.09 = 4.8921 \end{cases}$
	$\text{bH} + 0.31$	
	$\text{cO} - 0.31$	
	$\text{dO} - 0.31$	
		Theor. Mol. Stand. = 18.8870
		Depression for two H—O bonds = 1.34
		17.55
		Experimental Molecular = 16.73
		Difference 0.82

This second structure contains the covalency O—O link, which probably gives a depression greater than 2. Thus the difference 0.82 obtained with the second formula is considerably smaller than the combined depression due to polymerisation and bond O—O. Accordingly, diamagnetism decides clearly in favour of the formula with the co-ordinate O→O link. The above value 16.73 was measured in this department by Farquharson,⁶ with a Curie-Chéneveau Magnetic Balance.

One of us (J. H. C.) wishes to express his thanks to the Carnegie Trust for a Scholarship.

Summary.

Two existing diamagnetic standards (Pauling's theoretical and Pascal's experimental) are shown to be reconcilable, and their usefulness is enhanced

and demonstrated in a diamagnetic study of structure by a new plan, linking up diamagnetism with dipole moments and other properties, and applicable to a wide range of problems.

For benzene, naphthalene, acid carboxyl group, water and hydrogen peroxide, structures are given showing close quantitative agreement with diamagnetic data. The present plan differentiates precisely between different structures, including those involving resonance, and is applicable to cases for which no method has hitherto been available. Incidentally, an interpretation is given showing the theoretical significance of Pascal's rules obtained by him empirically.

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THE PROPERTIES OF DETERGENT SOLUTIONS. PART I.—THE INFLUENCE OF HYDROGEN ION CONCENTRATION ON THE SURFACE TENSION OF SOAP SOLUTIONS.

By J. POWNEY.

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Although it is known that the addition of alkalis can produce considerable changes in the surface tension of soap solutions, there appears to be very little data in the literature concerning this effect.

Bottazzi¹ has made observations on the changes of surface tension, viscosity and appearance of soap solutions which occur when acids and alkalis are added. His results, however, are complicated by the fact that the concentrations of soap used were in many cases so high that only partial solution of the soap was obtained. In general, it was found that the addition of sodium hydroxide produced an increase of surface tension, and that the subsequent addition of hydrochloric acid caused the surface tension to revert to its initial value. White and Marden² have also observed an increase of surface tension of soap solutions when alkali is added but little quantitative information is given.

In connection with a study of the physiological action of soaps, Jarisch³ has made some interesting observations on the surface tension and turbidity of very dilute buffered soap solutions, whilst Lottermoser and Tesch,⁴ using the stalagmometric method, have found that the form of the surface tension-concentration curves is altered if a few drops of alkali are added to the soap solution.

The question is one of considerable importance in the study of problems relating to detergent action, and it is in this connection that the present work has been carried out.

Recent researches on the properties of soaps and other long chain salts at relatively high dilutions indicate that such solutions have not the simple constitution that was formerly assigned to them. In par-

¹ Bottazzi, *Atti R. Acad. Lincei*, 1913, 21, II., 365.

² White and Marden, *J. Physic. Chem.*, 1920, 617.

³ Jarisch, *Biochem. Z.*, 1922, 134, 163.

⁴ Lottermoser and Tesch, *Koll. Beihefte*, 1931, 34, 339.

ticular, the very abrupt changes observed in the conductivity-concentration curves ⁵ and surface tension-concentration curves ⁶ have led to the suggestion that aggregation increases rapidly at the concentrations corresponding to the observed sharp changes in surface tension and conductivity. Murray and Hartley ⁷ have further shown that the transition from simple molecules to micelles would be expected to increase rapidly with concentration.

A knowledge of the general constitution of soap solutions at these critical concentrations, and the nature of the surface active species in particular, is of outstanding importance in connection with the study of detergent action, since it is exactly these concentrations which are most commonly used in detergent processes.

The present investigation has shown that profound changes in the surface tension of dilute soap solutions are brought about by comparatively small changes of hydrogen-ion concentration. Apart from the practical significance of this effect, it is hoped that a more extensive examination of the effect of p_H on the surface tension of dilute solutions of soaps, salts of alkyl sulphuric acids and alkyl aromatic sulphonates may assist in the interpretation of previous work.

Experimental.

Preparation of Soaps.—Pure sodium and potassium soaps of oleic, lauric and myristic acids were prepared in the following manner, particular attention being paid to the elimination of free alkali. A known weight (5-10 gm.) of fatty acid, obtained from British Drug Houses Ltd. and having a purity of 95 per cent. or better, was dissolved in 500 c.c. of hot absolute alcohol which had previously been redistilled over caustic soda and quick lime. The estimated amount of an alcoholic solution of caustic soda (or potash) was slowly added together with a minimum amount of phenol phthalein necessary to give a rough check of the neutral point. In the case of the saturated fatty acid soaps, the pure soap was recovered by distilling off the alcohol under reduced pressure, and allowing a slow stream of dry CO_2 free air to flow through the apparatus. The air stream was omitted in the case of the oleates, which are subject to oxidation.

Samples of the soaps were tested for loss of weight on continued heating at 105° C., and the free hydroxide or free fatty acid was estimated by dissolving 0.5 gm. soap in 150 c.c. hot absolute alcohol and titrating with standard acid or alkali. Further samples were tested for total alkali by decomposing a known weight of soap with excess standard acid. The fatty acid was removed by extraction with ether, and the aqueous layer titrated with standard caustic soda. In all cases the soaps had a purity of 99 per cent. or better. The maximum concentration of free hydroxide found was 0.06 per cent.

Surface Tension Measurements.—The ring method of measurement using a torsion balance of the du Noüy type in conjunction with a platinum ring was employed. This method is of particular value where rapid determinations of relative surface tensions are required rather than exact absolute values.⁸ All measurements were made at 20° C., and the values given are essentially static values, except possibly in the case of the lower concentrations where a continuous slow drift was sometimes found to occur, presumably due to the influence of atmospheric carbon dioxide.

⁵ Ekwall, *Z. physikal. Chem.*, 1932, **161**, 195.

⁶ Lottermoser and Puschel, *Koll. Z.*, 1933, **63**, 175.

⁷ Murray and Hartley, *Trans. Faraday Soc.*, 1935, **31**, 183.

⁸ See Lecompte Du Noüy, *Nature*, 1935, **135**, 397.

This latter effect has recently been investigated by Lottermoser.⁹ In this connection we have found that when a dilute soap solution is exposed to air, the p_H of the solution decreases appreciably. This might account for the observed slow change in surface tension. Deviations due to carbon dioxide can be minimised if surface tension measurements are made within three minutes of forming the surface. This period is quite sufficient to ensure normal surface equilibrium being reached. Redistilled CO_2 -free water was used for all solutions.

It was found that the angle of contact between a clean "flamed" platinum wire and the soap solutions used in these experiments was inappreciable and no corrections were therefore made to the surface tension readings.

Determination of p_H .—The use of indicators for determining p_H values of solutions of soap and other long chain salts may lead to erroneous results, as has been shown by several workers.¹⁰

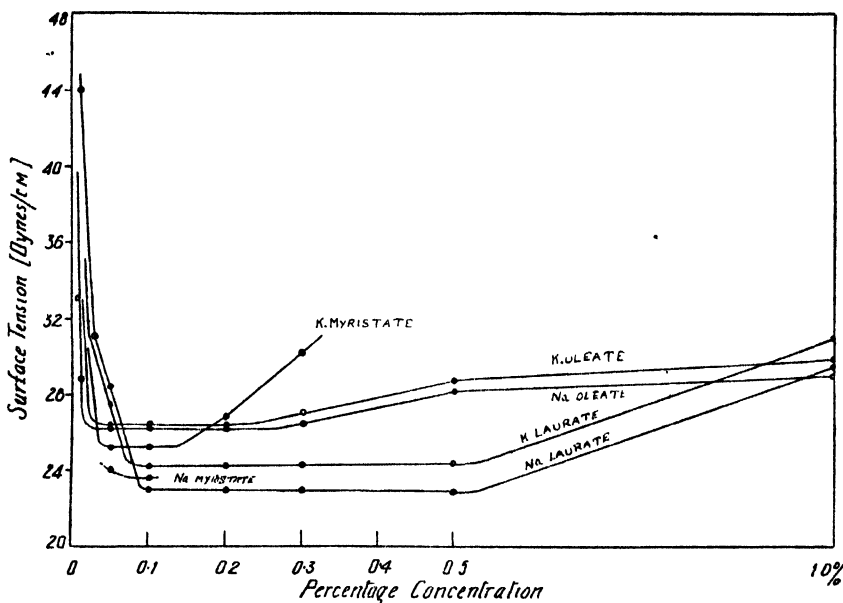


FIG. 1.—Surface tension-concentration curves (20° C.).

The present measurements were made by means of a glass electrode of the type developed by Morton.¹¹ The electrode was used in conjunction with a triode electrometer valve and two-stage amplifier, the circuit arrangement being similar to that described by Harrison.¹² This method has the important advantage that measurements can be made within two minutes, and furthermore it appears to have none of the disadvantages associated with indicators and the hydrogen electrode. The glass electrode was calibrated against standard Sørensen glycine-sodium hydroxide buffer solutions, and also against glycine-potassium hydroxide buffer solutions which were previously standardised by means of a hydrogen electrode. This second calibration was necessary since

⁹ Lottermoser, *Trans. Faraday Soc.*, 1935, **31**, 200.

¹⁰ Mosher, *American Dyestuffs Reporter*, 1930, **19**, 261; Hartley, *Trans. Faraday Soc.*, 1934, **30**, 444.

¹¹ Morton, *J. Sci. Inst.*, 1930, **7**, 187.

¹² Harrison, *J. Chem. Soc.*, 1930, 1528.

the characteristics of a glass electrode are to some extent dependent upon the nature of the cations present. Reproducible results were obtainable to an accuracy of ± 0.02 p_H units.

Results.

I. Surface Tension—Concentration Relationship.

The variations of surface tension with concentration for the sodium and potassium salts of oleic, lauric and myristic acids have been determined at 20°C . in the presence of atmospheric CO_2 , and the experimental curves are shown in Fig. 1. The order of maximum surface activity is approximately the same as that found by Madsen¹³ at 30°C . No irregularities were found in the curves corresponding to those observed by Lottermoser and Schladitz¹⁴ at higher temperatures.

The very low values of surface tension found for the laurates are of interest. The minimum surface tension for sodium laurate was found to be 23 dynes/cm. at a concentration of 0.1 per cent.

This value is practically the same as that found by Lottermoser and Schladitz¹⁴ at $30^\circ\text{--}50^\circ\text{C}$. in the presence of atmospheric CO_2 . In a more recent paper Lottermoser⁹ gives a value of approximately 53 dynes/cm. for an 0.1 per cent. solution of sodium laurate at 40°C ., and in the absence of CO_2 . It will be shown later that the considerable divergence between these two values can be attributed entirely to a small change of p_H consequent upon the absorption of atmospheric CO_2 .

The magnitude of the CO_2 effect is in many cases so large that any data for the surface tension of soap solutions are of little value unless the

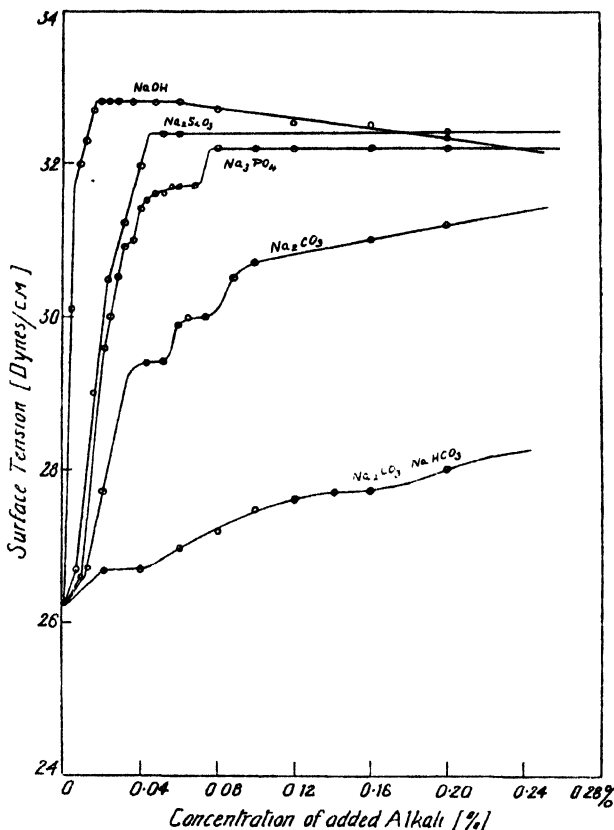


FIG. 2.—Effect of added alkalis on the surface tension of 0.1 per cent. sodium oleate solutions.

¹³ Madsen, *Detergent Action and Surface Activity* (Copenhagen, 1931).

¹⁴ Lottermoser and Schladitz, *Koll. Z.*, 1933, **63**, 295.

exact conditions of the experiment, and the p_H value of the solutions at the time of measuring the surface tension, are stated. It must be emphasised that the surface tension-concentration curves shown in Fig. 1 are those obtained in the presence of CO_2 . The results given are in substantial agreement with those obtained by other investigators under similar conditions, but they do not represent the "true" values of surface tension which are obtained only in the absence of CO_2 . The curves are chiefly of interest as a basis of comparison for the results given later in this paper concerning the influence of alkalis on surface tension.

II. Influence of p_H on Surface Tension.

The change of surface tension of soap solutions produced by the

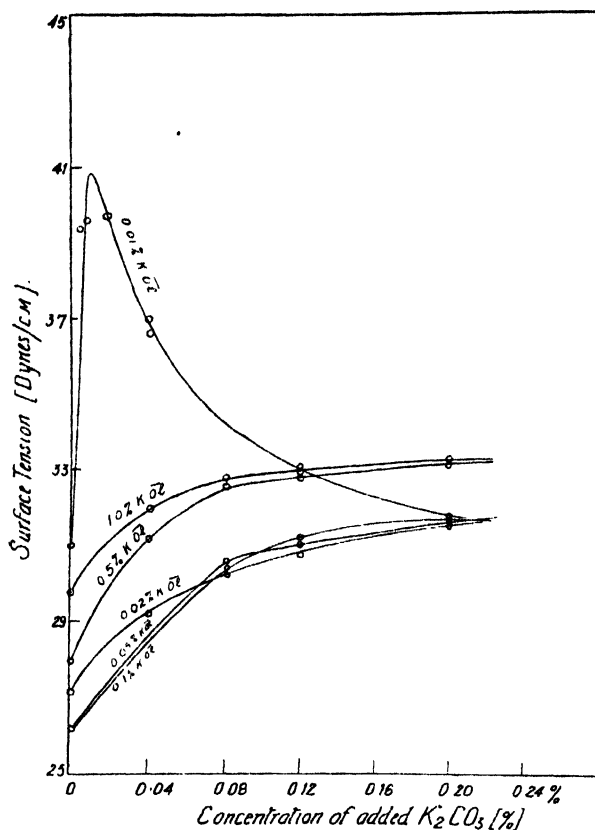


FIG. 3.—Change of surface tension of potassium oleate solutions on the addition of K_2CO_3 .

carbonate on the surface tension of 0.1 per cent. sodium oleate solutions. The alkali concentrations are given in terms of the anhydrous salts.

It will be seen that small concentrations (c. 0.04 per cent.) of the stronger alkalis produce a very rapid increase in surface tension. From 0.04 per cent. to 0.4 per cent. alkali the surface tension remains practically constant except in the case of sodium hydroxide where there is a slight decrease with increasing alkali concentration. The weaker alkalis produce a much less pronounced effect but in all cases there is a tendency for the surface tension to rise with increasing concentration of alkali.

addition of alkalis has been studied. The method employed was to add from a micro-burette successive small amounts of a concentrated alkali solution to the soap solutions. The solution was well stirred and its surface tension determined after each addition of alkali. The volume of alkali solution added was so small that dilution of the soap solution could be neglected.

(a) Oleates.

In Fig. 2 is shown the effect of sodium hydroxide, sodium metasilicate, trisodium phosphate, sodium carbonate and sodium sesqui-

cent. sodium chloride was added to an 0.1 per cent. sodium oleate solution. If, however, alkali was first added until the maximum surface tension was attained, and sodium chloride then added, it was found that a small but definite *decrease* of surface tension occurred.

The experimental curve shown in Fig. 4 is a composite one built up from the surface tension- p_H curves obtained for the individual alkalis. With the exception of the NaOH curve, which is slightly displaced, the curves run together in a satisfactory manner. The divergence of the NaOH

curve is probably due to the low buffering action of the very small quantity of NaOH used to obtain the lower p_H values.

The surface tension reaches a definite maximum at about $p_H = 12$. Between $p_H = 10.3$ and $p_H = 9.7$ there appeared to be an extremely sensitive region in which the surface tension tended to reach a second sharp maximum at approximately $p_H = 10$.

Over the range $p_H 9.5 - p_H 8.2$ the surface tension assumes its normal value, except for a slight decrease between $p_H 8.9 - p_H 8.2$. This decrease occurs just before the limit of stability is reached. Below $p_H 8.2$ the solution becomes turbid

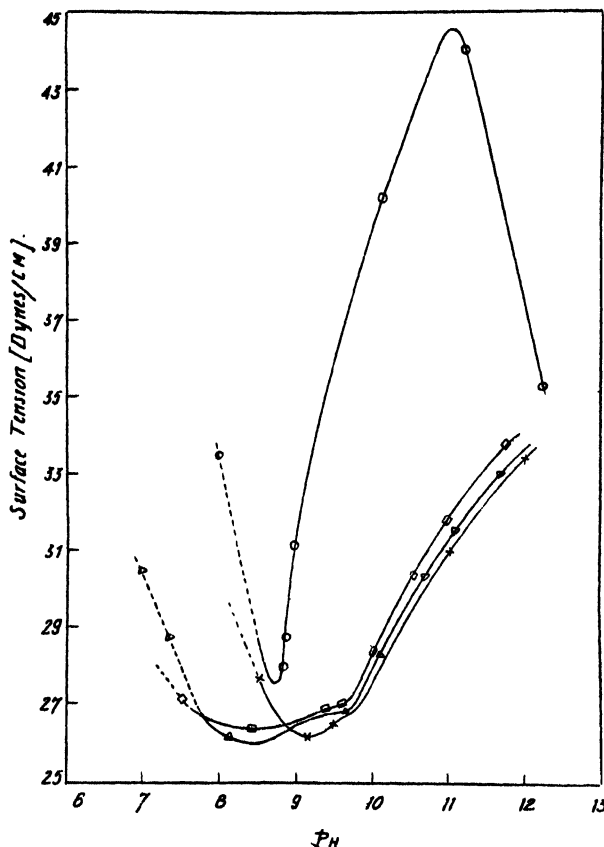


FIG. 5.—Surface tension- p_H curves for buffered K. oleate solutions.

0.25 per cent. K. oleate	.	.	□
0.10 " " "	.	.	△
0.05 " " "	.	.	×
0.01 " " "	.	.	○
Turbidity " "	.	.	---

owing to the separation of fatty acid or acid soap, and a sharp increase of surface tension takes place.

The surface tension- p_H curves obtained for potassium oleate solutions of various concentrations are given in Fig. 5. In these experiments potassium phosphate buffer solutions consisting of mixtures of K_2PO_4 , K_2HPO_4 , and KH_2PO_4 were used to cover the p_H range. The total salt concentration of the buffers was in each case 0.25 per cent.

It will be seen that the influence of p_H on surface tension becomes

very marked at a concentration of 0.01 per cent. potassium oleate. The sensitive region at p_H 10 observed for sodium oleate solutions containing small quantities of alkali was not found for potassium oleate solutions which were definitely buffered with phosphate mixtures.

(b) Laurates.

In connection with the surface tension-concentration curves for the laurates, it was stated that the very low minimum values of surface tension could only be obtained if precautions were taken to eliminate all traces of

alkali other than that produced by hydrolytic dissociation. The reason for this is clearly demonstrated in Fig. 6 which shows the effect of potassium carbonate on the surface tension of potassium laurate solutions. Similar curves were obtained using sodium laurate solutions and sodium carbonate. The enormous increase of surface tension of an 0.1 per cent. potassium laurate solution from 23 dynes/cm. to 53 dynes/cm. produced by 0.004 per cent. of K_2CO_3 is most remarkable. The change at lower soap concentrations is even greater, the maximum surface tension approaching that of water.

With increasing concentration of potassium laurate, the effect of alkali decreases rapidly. Any addition of alkali in excess of that required to give the maximum value of surface tension results in a gradual linear decrease of surface tension.

The corresponding surface tension — p_H curves for potassium laurate solutions are shown in Fig. 7. The reason for the considerable difference in the values of surface tension of laurate solutions observed in the presence of CO_2 , and in a CO_2 -free atmosphere is now evident from these curves.

If the value of 53 dynes/cm. found by Lottermoser for 0.1 per cent. sodium laurate in the absence of CO_2 is taken as the "true" value, then

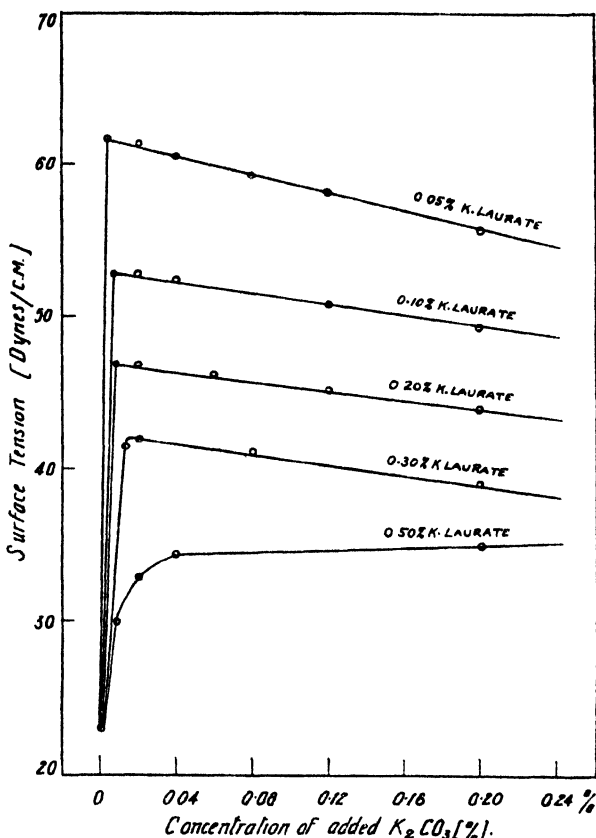


FIG. 6.—Influence of K_2CO_3 on the surface tension of potassium laurate solutions.

it will be seen from Fig. 7 that a decrease of p_H of approximately 1.5 units will cause a decrease of surface tension to the value of 23 dynes/cm. found in the presence of CO_2 . That such a decrease of p_H can occur is shown by an experiment we have made in which it was found that the p_H of an 0.1 per cent. sodium laurate solution decreased from $p_H = 9.1$ to $p_H = 7.7$ on exposure to air, the solution eventually becoming turbid.

The very rapid increase of surface tension of potassium laurate solutions produced by the addition of very small quantities of alkali (see Fig. 6) can be considered as a reversal of the CO_2 effect. The sharp maximum values obtained with traces of alkali correspond to the true surface tension

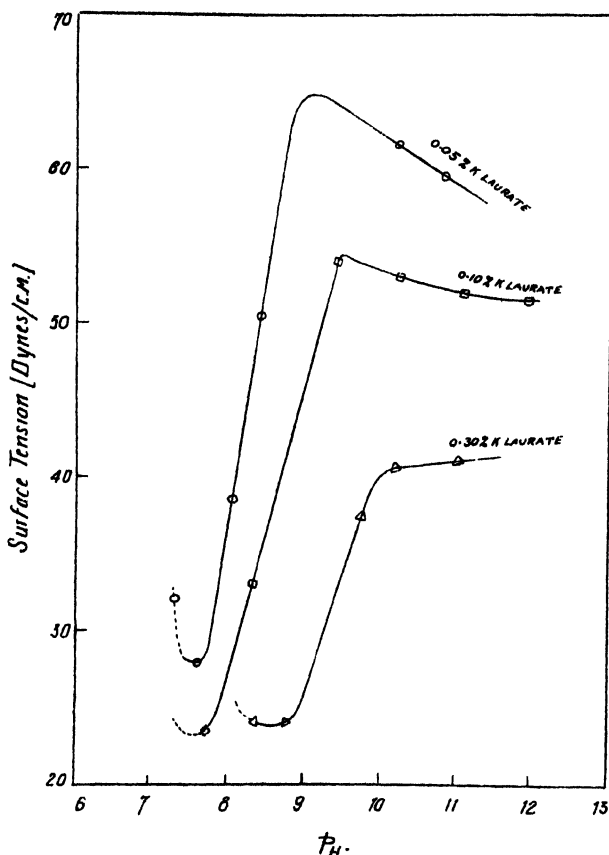


FIG. 7.—Surface tension— p_H curves for potassium laurate solutions.

values which would be obtained in the absence of CO_2 . This is clearly shown in Fig. 8, where the normal surface tension-concentration curve for potassium laurate in the presence of CO_2 is shown plotted together with a curve based on Lottermoser's data for the surface tension of sodium laurate solutions in the absence of CO_2 , and a third curve showing the maximum values of surface tension produced by traces of alkali (see Fig. 6) at various concentrations of potassium laurate. The agreement between the last two curves is very satisfactory

when it is taken into account that Lottermoser's data refer to a somewhat higher temperature. The displacement between the two upper curves and the normal surface tension concentration curve represents the magnitude of the CO_2 effect at different potassium laurate concentrations.

The conclusions that have been reached in regard to the laurates also apply to the other soaps. In general, if the influence of CO_2 on surface tension is small, then the elevation of surface tension (in the presence of CO_2) produced by alkalis will be small, and vice versa. It is hoped shortly to study the influence of alkalis on surface tension in the absence of CO_2 . It may be expected that the general effect will be to produce a

slight decrease of surface tension as indicated by the decrease of surface tension which occurs after the sharp maximum has been reached (Fig. 6).

(c) **Myristates.**

Owing to the limited solubility of the myristates at 20° C. only the potassium salt was studied. The addition of alkali produced a relatively small increase of surface tension of potassium myristate solutions at concentrations greater than 0.1 per cent. At 0.02 per cent. concentration, however, the effect once more became very pronounced, although the maximum observed values of surface tension were rather less than those found for the laurates.

Discussion of Results.

The remarkable effect of alkalies on the surface tension of sodium and potassium laurate solutions bears a close resemblance to a so far unexplained phenomenon observed by Harkins and Clark,¹⁸ who found that the addition of a small amount of NaOH increased the surface tension of an 0.1 M solution of sodium nonylate from 20.2 dynes/cm. to 45.4 dynes/cm. Further addition of NaOH caused a linear decrease of surface tension. They attribute the normal low

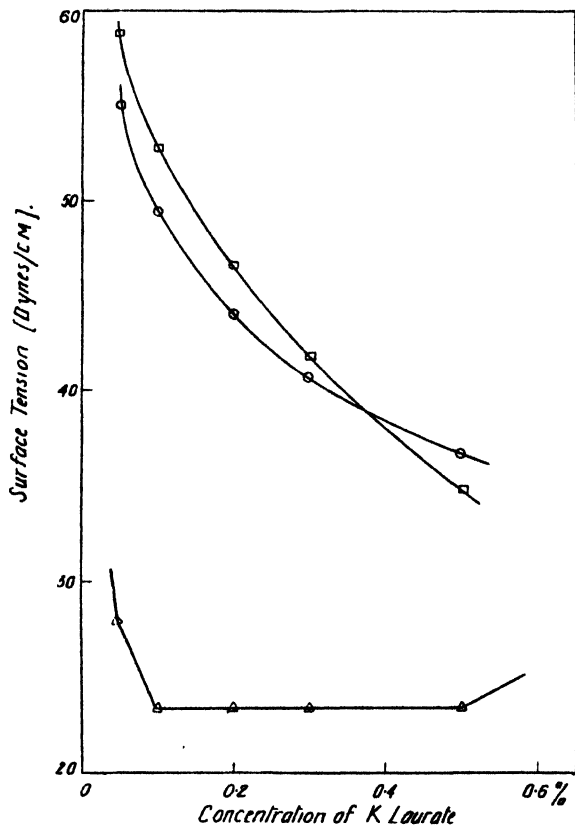


FIG. 8.—
 ▲ Surface tension of K. laurate in presence of CO₂.
 □ Surface tension of Na. laurate in absence of CO₂ (Lottermoser).
 ○ Maximum values of surface tension of K. laurate solutions on addition of K₂CO₃.

value of surface tension to a surface film of the salt together with nonylic acid produced by hydrolysis, the rapid increase caused by the addition of alkali being due to suppression of hydrolysis and consequent removal of free fatty acid.

The present work indicates that the effect observed by Harkins and Clark is not peculiar to sodium nonylate, but is also characteristic

of laurates, myristates and oleates, being most pronounced in the laurates.

The surface tension becomes increasingly sensitive to changes of p_H as the concentration of soap approaches that at which the sharp change in the surface tension-concentration curve occurs. According to Harkins and Clark, the percentage hydrolysis is at a maximum in this region. This might indicate that the phenomenon is directly connected with suppression of hydrolysis. It is not clear, however, why the maximum surface tension elevation produced by alkalis should fall off so rapidly with increasing soap concentration, unless there is a critical soap concentration at which the free fatty acid becomes aggregated in a micelle of the type $(HX)_n X_m^{m(-)}$ or forms an acid soap $n \cdot NaX - m \cdot HX$.

According to Tyutyunnikov and Kas'yanova¹⁶ there are considerable divergences between the observed and calculated OH-ion concentrations of dilute soap solutions containing alkali. With increasing amounts of alkali the concentration of OH-ions adsorbed by the soap increases rapidly until a certain p_H is attained, after which it suddenly falls. The value of the critical p_H depends upon the nature of the soap. This effect bears a close resemblance to the present observations on the rapid increase of surface tension with increasing p_H , particularly in respect to the subsequent decrease of surface tension above a certain critical p_H . If a direct relationship exists between the two phenomena then it would appear that the increase of surface tension produced by alkalis is brought about by adsorption of OH-ions by the surface active constituent of the soap solution, either with or without change in the state of aggregation.

Murray¹⁷ has recently suggested that it is the simple long chain ions which are responsible for the surface activity of colloidal electrolytes. Owing to their highly localised charge, the unaggregated ions will be subject to orientation at a water-air interface. The ionic micelle, however, will have a completely hydrophilic exterior, on account of its uniformly distributed charge, and will have a negligible surface activity.

On this hypothesis, the observed large increase of surface tension of dilute laurate solutions produced by small changes of p_H may possibly be accounted for if it is assumed that a trace of alkali can facilitate the transformation of single fatty acid ions into ionic micelles, either by modification of the surrounding ionic atmosphere or by some other process. Secondary dehydration effects may also be produced by the alkali.

If such an effect does occur, it might be expected that the physical nature of the surface would alter considerably. In this connection we have made some preliminary attempts to measure the surface viscosity of sodium laurate solutions by observing the damping of an oscillating disc placed in the surface. It was found that the damping produced by an 0.1 per cent. sodium laurate solution which had been exposed to atmospheric CO_2 ($\sigma = 23$ dynes/cm.) was extremely high, the surface appearing to be "semi-rigid." The addition of 0.004 per cent. Na_2CO_3 to the sodium laurate solution produced a remarkable decrease in surface viscosity, the damping now being practically identical with that found for water.

¹⁶ Tyutyunnikov and Kas'yanova, *Allgem. Oel-u. Fett-Ztg.*, 1934, 31, 276.

¹⁷ Murray, *Trans. Faraday Soc.*, 1935, 31, 206.

Although it is not possible at the present stage to form any definite conclusions concerning the mechanism whereby such considerable changes of surface tension are produced by relatively small changes of p_H , it would seem that any explanation based entirely on the suppression of hydrolysis does not adequately account for the observed phenomena.

We hope shortly to investigate the influence of hydrogen-ion concentration on the surface tension of solutions of long chain alkyl sulphates and alkyl aromatic sulphonates. With these compounds there are no complications due to hydrolysis and it should be possible to determine whether the p_H effect observed for soaps is entirely connected with hydrolysis or if there are other factors concerned. It is thought that the very interesting observations recently made by Adam and Shute¹⁸ on the slow drift of surface tension which occurs with solutions of alkyl pyridinium and alkyl trimethyl ammonium bromides may possibly be connected with a change of p_H produced by atmospheric CO_2 .

Summary.

The surface tensions of solutions of the sodium and potassium salts of oleic, lauric and myristic acids have been determined at 20° C., in the presence of atmospheric CO_2 .

The change of surface tension produced by added alkalies, and by changes of p_H in general, has been investigated. It is found that small changes of p_H can produce very considerable changes of surface tension. The laurates are particularly sensitive in this respect.

The influence of carbon dioxide on the surface tension of soap solutions can be correlated with changes of p_H produced by adsorption of CO_2 .

Finally, I wish to express my thanks to Mr. J. T. Holden, B.Sc., for his valuable advice and encouragement, and to the other members of this laboratory for their helpful co-operation.

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¹⁸ Adam and Shute, *Trans. Faraday Soc.*, 1935, 31, 204.

THE DECOMPOSITION OF CHLORAL CATALYSED BY NITRIC OXIDE.

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In a previous paper¹ the decomposition of chloral catalysed by iodine was reported. In this case the data did not definitely distinguish whether the catalyst was the iodine molecule or the iodine atom. In the course of a larger programme dealing with the homogeneous catalysis of gaseous decompositions, the decomposition of chloral catalysed by nitric

¹ Verhoek and Hinshelwood, *Proc. Roy. Soc.*, 1934, 146A, 334.

oxide was investigated to throw further light on this problem. The catalysed decomposition is readily studied in the neighbourhood of 400° C.

Nitric oxide was prepared by a modification of the method of Noyes² by dropping 35 per cent. sulphuric acid into a 40 per cent. solution of sodium nitrite, bubbling the gas through concentrated sulphuric acid and a trap in acetone and solid carbon dioxide, and storing over mercury covered with a layer of sulphuric acid. The chloral used was the commercial preparation.

The apparatus was the same as that used in the previous study, with a silica bulb in the well of an electrically-heated furnace connected to a capillary mercury manometer on which the rate of increase of pressure was observed. Chloral was put into the bulb first, and then nitric oxide. By filling a part of the connecting tubes to a suitable pressure with the latter, it could be introduced into the reaction vessel almost instantaneously by turning a stop-cock, so that there was no uncertainty about the zero time of the experiment.

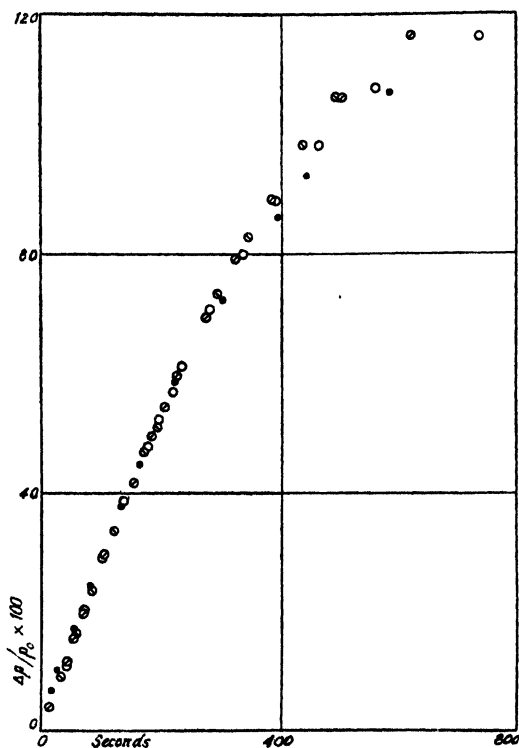


FIG. 1.—Affine curves for the decomposition of chloral catalysed by nitric oxide.

Symbol.	P_{NO}	P_{CCl_3CHO}	t_{50}
○	47	98	347
○	92	101	188
○	312	109	54
●	92	29	154

92 mm. NO and 101 mm. CCl_3CHO , which is unaltered. The curves are evidently affine, showing that the nature of the reaction is unchanged by changing the ratios of the two substances.

The time for a definite percentage increase in pressure (50 per cent.) may then be used as a measure of the reaction rate. The initial nearly straight portion of the curve now goes to a greater percentage increase before bending over than with the uncatalysed reaction, suggesting that

² W. A. Noyes, *J. Amer. Chem. Soc.*, 1925, 47, 2170.

the catalytic effect of nitric oxide on the decomposition of the chloroform formed as a primary product is somewhat different from its effect on the decomposition of chloral. At any rate, it indicates that the decomposition of chloroform is catalysed by nitric oxide, a fact which was confirmed by direct experiment with nitric oxide and chloroform. As in the case of the iodine catalysis, therefore, it is a question of the catalysis of the chloral-chloroform system, rather than of chloral alone.

The catalysed reaction is first order with respect to chloral over a ten-fold range of initial pressures, at a constant pressure of nitric oxide, as shown in Table I.

TABLE I.—VARIATION OF THE REACTION RATE WITH THE PRESSURE OF CHLORAL AT 401°.

p_{NO} (mm.) . . .	92	92	92	91	98	103
$p_{\text{CCl}_3\text{CHO}}$ (mm.) . .	29	45	101	102	203	298
t_{50} (sec.) . . .	154	162	188	181	178	178

The reaction velocity is directly proportional to the pressure of nitric oxide, as shown in Fig. 2, where the reciprocal of the time for 50 per cent. increase in pressure for experiments with 100 mm. CCl_3CHO is plotted against the pressure of nitric oxide.

The rate of the catalysed decomposition was determined for four temperatures over a range of 65° to determine the energy of activation, keeping the concentrations of nitric oxide and chloral constant. The data are given in Table II.

Using average values of t_{50} at each temperature, a straight line is obtained when $\log t_{50}$ is plotted against $1/T$, from the slope of which the energy of activation is calculated to be 37,100 calories per gram molecule. This is somewhat less than the value for the catalysis by iodine.

From the relation between the rate and the concentration of catalyst, and using the fact that the reaction is first order with respect to chloral, it may be calculated that the number of chloral molecules reacting per c.c. per sec. at 401° when the pressures of chloral and nitric oxide are each 100 mm. is 6.13×10^{15} . The number of molecules decomposing as a result of the uncatalysed reaction is less than one-tenth of this at this temperature, and may be neglected. The number of collisions between chloral molecules and nitric oxide molecules under these conditions is 8.72×10^{36} per c.c. per sec., using the value 3.4×10^{-8} for the diameter of the nitric oxide molecule and assuming 5×10^{-8} for the diameter of the chloral molecule. If only two squared terms are involved

in the reaction, multiplication of this value by $e^{-\frac{37100}{RT}}$ should give the reaction rate. The value of the product is 8.14×10^{14} . This is about one-seventh of the number of molecules reacting, and seems to show

TABLE II.—INFLUENCE OF TEMPERATURE ON THE DECOMPOSITION OF CHLORAL CATALYSED BY NITRIC OXIDE.

T (°Abs.).	p_{NO}	$p_{\text{CCl}_3\text{CHO}}$	t_{50}
629	88	102	1246
	90	94	1190
649	90	102	494
	91	100	501
674	93	98	158
	93	103	157
	92	100	185
	91	104	181
694	93	99	70
	94	99	72
	93	99	81
	95	95	79

that two squared terms are sufficient to account for the rate of the catalysed reaction. The agreement is not quite good enough, however, to allow one to say definitely that only two squared terms are involved, and thus to give an unequivocal answer to the question of catalysis by iodine molecules or iodine atoms discussed in the previous paper.

Nitrous oxide, and small amounts of oxygen (introduced as air) have no detectable effects on the decomposition of chloral. Larger amounts of oxygen, however, appear to accelerate the decomposition. Thus, while experiments in the presence of 1 mm. of air and 10 mm. of air showed the same rate as for the reaction without air, the time for 50 per cent. increase in pressure with 99 mm. of air was 74 per cent. of the normal value. The absence of any catalysis by nitrous oxide and by small amounts of air in the case of chloral is in striking contrast to their

effects on the decomposition of acetaldehyde discussed in the following paper.

The decomposition of chloral catalysed by nitric oxide is interesting as exhibiting simple relationships between the rate of decomposition and the pressures of the two constituents. As in other cases, the essential feature of the catalysis seems to be the reduction of the energy of activation and of the number of squared terms necessary to account for the rate of activation. It is not clear how this is brought about by nitric oxide. For other reacting systems it has been suggested that paramagnetic sub-

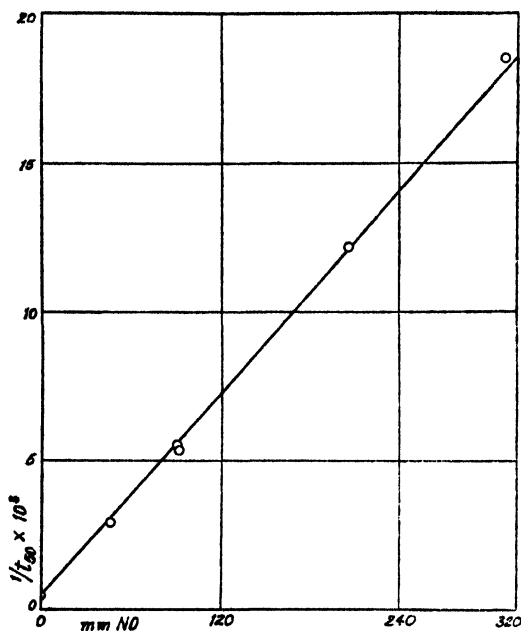


FIG. 2.—Variation of the reaction rate with the pressure of nitric oxide.

stances exert a catalytic effect on the reactions, but if it is the paramagnetic property of nitric oxide which makes it effective, one would have expected a greater effect with the more strongly paramagnetic oxygen. It is suggested elsewhere that the effect of nitric oxide on the decomposition of acetaldehyde is connected with an oxidation of the acetaldehyde by nitric oxide, but this mechanism is excluded here by the negative results with nitrous oxide and oxygen. It may be that the nitric oxide molecule, with its odd electron, exerts a perturbing influence on the chloral molecule, so that the binding forces in the latter when it is close to a nitric oxide molecule have values appreciably different from those when it is by itself.

APPENDIX.

The Decomposition of Chloroform and its Catalysis.

In the course of an investigation of the decomposition of chloral,¹ it was found necessary to obtain some data on the decomposition of chloroform. It was observed that the reaction was catalysed by iodine, by nitric oxide, and by the reaction products. That the decomposition of such a simple molecule should be subject to catalysis was somewhat surprising, and it was thought worth while to study it a little further.

Chloroform was purified by letting it stand for some time over calcium chloride to remove the alcohol preservative, and distilling. The apparatus used was the same as that for chloral.

Chloroform decomposes rapidly at 512° C., giving a pressure increase of about 55 per cent. The curve of pressure increase against time has an odd shape with three points of inflection. Fig. 3 shows such a curve for an experiment in which the initial pressure was 244 mm. The products contain hydrogen chloride, a dirty solid, presumably hexachloroethane,

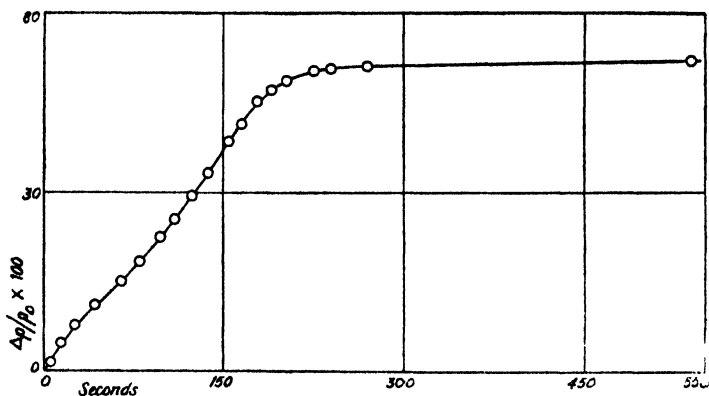


FIG. 3.—The decomposition of chloroform at 512°.

which condenses in the cooler parts of the apparatus, and tar. All the hydrogen appears as hydrogen chloride; (analyses at the end-point gave 1.07, 1.11, and 1.10 mm. HCl per millimeter of chloroform originally present, which in view of experimental difficulties is as near as can be expected to the theoretical 1.0 mm.).

The reaction does not lend itself to accurate study, but on plotting the reciprocal of the time for 25 per cent. increase in pressure, as given in Table I. against the initial pressure, a nearly horizontal straight line is obtained from 50 mm. to 300 mm., indicating that the reaction is closely first order over this range. At pressures lower than 50 mm. the points are scattered, but there are signs that the reaction rate has begun to decrease when the pressure reaches 30 mm.

TABLE I.—THE DECOMPOSITION OF CHLOROFORM AT 512°.

p_0 (mm.)	7.5	15	20	20.5	25	30	39.5
t_{25} (sec.)	105	145	128	115	136	159	144
p_0 (mm.)	56	100	107	164	185	244	287
t_{25} (sec.)	106	120	105	100	108	108	105

Dry hydrogen chloride has no effect on the decomposition. The other decomposition products have a catalytic effect roughly proportional to the

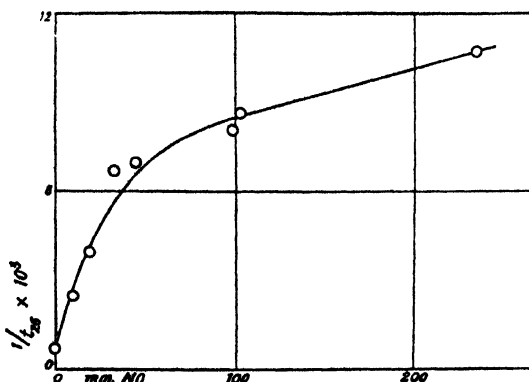


FIG. 4.—The decomposition of chloroform catalysed by nitric oxide at 452°.

ratio of the concentration of the products to the concentration of chloroform, as may be seen by plotting the reciprocal of the time for 25 per cent. increase against this ratio. The reaction products were prepared *in situ* by allowing chloroform to decompose. The data are given in Table II. The catalytic effect of nitric oxide is greater than that of the decomposition products, and was studied at 452°. Fig. 4 shows the curve obtained for the variation of the rate with the pressure of nitric oxide. This is particularly interesting as an example of a catalysis showing a non-linear variation with the catalyst in which the reality of the non-linearity is not rendered uncertain by the possible existence of two species of catalyst as with iodine (atoms or molecules), or by complicating factors as with acetaldehyde and nitric oxide.

From the value of t_{25} for the uncatalysed decomposition at 512° and 452° an energy of activation is calculated with a value of 49,000 calories per gram molecule.

The author wishes to thank Mr. C. N. Hinshelwood for help and assistance.

TABLE II.—THE DECOMPOSITION OF CHLOROFORM CATALYSED BY ITS DECOMPOSITION PRODUCTS AT 512°.

p_0 (mm.).	Decomposition Products (mm.).	Decomposition Product $\frac{p_0}{p_0 - p}$.	t_{25} (sec.).
32.5	30	0.92	94
34.5	81	2.35	62
111	13	0.12	111
98	22	0.22	121
112	60.5	0.54	122
129	130	1.01	74
116	165	1.42	70
119	191	1.60	65
109	268	2.46	61
109	336	3.08	53
93	425	4.56	46

Summary.

The decomposition of chloral is catalysed by nitric oxide. The catalysed reaction is of the first order with respect to chloral, and the rate increases in direct proportion to the concentration of nitric oxide. Nitrous oxide and small amounts of oxygen have no catalytic effect on the decomposition. The mechanism of the catalysis is discussed.

The rate of decomposition of chloroform at 512° is found to be nearly first order with respect to the initial pressure above 50 mm. The decomposition is catalysed by the decomposition products, and by nitric oxide.

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THE DECOMPOSITION OF ACETALDEHYDE CATALYSED BY NITROUS OXIDE.

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It was observed that in the presence of nitrous oxide, acetaldehyde undergoes a catalytic decomposition. The question immediately arose as to whether this was a direct catalysis or a chain reaction in which the chains were initiated by some sort of oxidation reaction. The same question arises in considering the decomposition in the presence of oxygen, small amounts of which cause the decomposition of much larger quantities of acetaldehyde than can be accounted for by a simple oxidation. With oxygen the experimental difficulties are increased by the fact that the oxygen is rapidly used up by the reaction; with nitrous oxide this is not so, and the nitrous oxide-acetaldehyde reaction seemed a useful one for detailed study.

In a clean silica vessel, the catalytic decomposition is complicated by a surface reaction. This surface reaction may be obviated by covering the walls of the vessel with a layer of carbon. The pressure increase-time curve referred to acetaldehyde for the remaining reaction is then found to be closely represented by an equation involving a $3/2$ power of the acetaldehyde, and the variation of the rate with the initial pressure of acetaldehyde at a constant pressure of nitrous oxide is given by a curve which rises rapidly at first and then bends over to rise with a more gentle slope. The rate varies nearly with the square root of the nitrous oxide pressure at a constant pressure of acetaldehyde. The reaction thus involves more than simply one molecule of each of the reactants, and the observed data may be explained by a mechanism involving the formation of some substance from the two reactants which then acts as a catalyst, or by a chain mechanism. The catalyst-forming or chain-initiating reaction between nitrous oxide and acetaldehyde is assumed to be an oxidation, thus making the catalysis analogous to what is to be expected for the catalysis by oxygen.

The catalyst mechanism proposed consists in the formation of some substance from nitrous oxide and acetaldehyde which then acts as a catalyst and decomposes acetaldehyde on collision with it. This catalyst is sometimes destroyed itself by collision with acetaldehyde, and by collision with nitrous oxide, and it is destroyed on collision with the walls of the reaction vessel. Under these conditions, and assuming that the concentration of the catalyst is constant in the steady state, the rate of disappearance of acetaldehyde is given by

$$-\frac{d[A]}{dt} = k_1[A][N_2O] + \frac{k_1(k_2 + k_3)[A]^2[N_2O]}{k_2[A] + k_4[N_2O] + k_5}$$

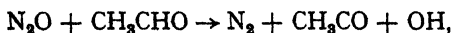
in which k_1 is the velocity constant for the formation of the catalyst, k_2 , k_4 and k_5 the constants for its destruction by collision with acetalde-

hyde, nitrous oxide, and the walls respectively, and k_2 the constant for the catalytic decomposition of acetaldehyde on collision with the catalyst. The first term on the right is small compared with the other and may be neglected. With a proper choice of constants the course of the pressure increase-time curve for a single reaction appears $3/2$ order, and the order is not greatly altered by wide variations in the concentrations of acetaldehyde and of nitrous oxide. The variation of the rate with the initial pressures of the two reactants is given by equations of the form

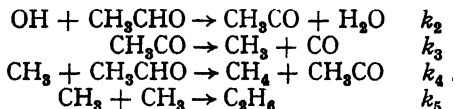
$$\frac{1}{t_4} \sim \frac{\text{Constant} \times [A]}{\text{Constant} + \text{Constant} \times [A]}, \quad \frac{1}{t_4} \sim \frac{\text{Constant} \times [N_2O]}{\text{Constant} + \text{Constant} \times [N_2O]},$$

which account reasonably well for the observed data.

If the catalyst formed from acetaldehyde and nitrous oxide is capable of decomposing large quantities of acetaldehyde before it is itself destroyed, the mechanism has definite analogies with a chain reaction. The similarity of the catalytic effects of oxygen and nitrous oxide, and the knowledge that the oxidation by oxygen at lower temperatures does involve chains, would also suggest a chain reaction. The initiating reaction for the catalytic chain may be assumed to be



with a velocity constant k_1 . The heat of this reaction is calculated to be endothermic, and equal to 31,100 calories. The reaction then proceeds according to steps similar to those suggested by Rice and Herzfeld¹ for the uncatalysed decomposition



The rate of reaction is found to be

$$-\frac{d[A]}{dt} = 2k_1[N_2O][A] + k_4\sqrt{\frac{2k_1[N_2O]}{k_5}}[A]^{\frac{3}{2}},$$

the first term being negligible in comparison with the second. The equation reproduces the $3/2$ power found for the course of the reaction, and the square root observed for the variation with the pressure of nitrous oxide. It does not, however, permit the variation of the rate with acetaldehyde to involve different constants from those required by the variation with nitrous oxide, as found experimentally. If the uncatalysed decomposition is also assumed to be a chain reaction, so that the observed decomposition is the combined result of chains initiated by two independent primary reactions, an additive constant term will be introduced under the radical sign and the variation with the two constituents will be different, but from a quantitative standpoint the change produced by this alteration is not sufficient to account for the observed difference.

The data of the investigation are given briefly in the following pages.

Kahlbaum's acetaldehyde, freshly distilled in a glass apparatus, was used. Nitrous oxide was prepared free from air by repeated fractionation in liquid air of commercial nitrous oxide for anaesthesia.

¹ F. O. Rice and Herzfeld, *J. Amer. Chem. Soc.*, 1934, **56**, 284.

Nature of the Reaction.

The reaction is a catalytic decomposition of acetaldehyde, and not a reaction between nitrous oxide and acetaldehyde, though the primary step in the catalysis may be such a reaction. The average value of the total pressure increase for several reactions with different pressures of nitrous oxide and acetaldehyde was 98½ per cent. of the initial pressure of acetaldehyde. This value shows no change with changes in the ratio of nitrous oxide to acetaldehyde.

The products of reaction contain carbon monoxide and methane, with no hydrogen, unsaturated hydrocarbons, nor carbon dioxide. Analyses of the products were made by condensing out one fraction of the gases in liquid air, and analysing the two fractions separately. The fraction condensed by liquid air contained no carbon dioxide, nor could carbon dioxide be detected as a turbidity on testing the products with baryta.

In view of the very marked catalytic effect of traces of oxygen, special experiments were made to ensure that the catalysis was not the result of a contamination of the nitrous oxide with oxygen. That this could be the case seemed unlikely from the fact that the addition of more acetaldehyde to the products of a previous reaction, in which the trace of oxygen should have been used up, showed the catalytic effect of the nitrous oxide to be unimpaired. To make still more certain, acetaldehyde was allowed to decompose in the presence of nitrogen containing a trace of oxygen. The dilution with the large amount of inert gas caused no change in the typical pressure increase-time curve for oxygen catalysis, which rises rapidly at first and then shades off as the oxygen is used up, and is very different from the curve for nitrous oxide and acetaldehyde.

Even though the nitrous oxide is not contaminated with oxygen initially, the catalysis might still be due to oxygen, if the oxygen were formed by a decomposition of nitrous oxide in the reaction mixture itself. It was found, however, that leaving nitrous oxide in the reaction bulb for periods four to ten times as great as the half-time formed no amounts of oxygen detectable in the rate of reaction nor as a change in the shape of the pressure increase-time curve. These experiments show that the nitrous oxide does not act as a preliminary source of oxygen; they do not exclude the possibility of its acting directly as an oxidising agent in a reaction with acetaldehyde.

If the reaction was in some measure an oxidation chain, it might be possible to slow it down by putting in some substance in the nature of an anti-knock. Aniline added to the reaction mixture in concentrations up to 5 per cent. of the acetaldehyde present, however, had no effect, either on the rate of decomposition in the presence of nitrous oxide, nor in the presence of oxygen.

A likely product of an oxidation reaction between acetaldehyde and nitrous oxide would be some acidic substance, whether acetic acid or some other. No evidence of the presence of acid in a water solution of the products could be found in repeated attempts.

The results of the experiments in this section are not in agreement with those of Steacie and McDonald,^a who find that on leaving acetaldehyde, at lower pressures than those used here, and nitrous oxide together for longer times at the lower temperature 450° an oxidation occurs, the final products being carbon dioxide and methane from the decomposition of acetic acid which is the primary product.

Effect of Surface.

The rate of reaction is greater when the surface of the reaction bulb is clean than when it is covered with carbon. The original value found for the half-life for a reaction mixture containing 100 mm. N_2O and 100 mm. CH_3CHO in a bulb which had been in use for some time was 885 sec.

^a Steacie and McDonald, *Can. J. Res.*, 1935, 12, 711.

After several days in which the bulb was used in this condition, air was inadvertently admitted to the bulb when it was at a high temperature. The half-time dropped to 187 sec., and then showed a steady trend, consecutive experiments giving for the half-time 187, 219, 243, 258, 262, 270 sec. The trend is probably the result of the deposition on the walls of small amounts of carbon. By allowing acetone to react in the bulb at 630° the walls were so covered with carbon that the half-life was even greater than the original value, becoming constant and unchanged by further treatment with acetone at 1195 sec., an average value for five experiments whose values fall within twenty seconds on either side of this. The data for the "dirty" bulb in the following are the original data, for which the half-life for the 100 : 100 mixture was 885 sec.

In view of the large effect on the half-life caused by covering the walls with carbon, one expected to find a great acceleration on passing to a packed bulb. This is not, however, the case. A bulb packed with silica balls, with a surface to volume ratio sixteen times that of the unpacked bulb, gave values of the half-time for successive experiments when clean : 53, 76, 93, 107, . . . sec. On treatment with acetone the half-life rose to a value twice as great as in the unpacked bulb, indicating a retardation by the increase of surface. These results are fairly well reproducible; on burning off the carbon with oxygen at a high temperature, the rate increases to its original "clean" value. The end-points do not change with the state of the bulb.

The Reaction in a "Clean" Bulb.

The effect of varying the concentrations of the components of the mixture in a clean bulb shows that the reaction half-time is independent of the acetaldehyde concentration at a constant concentration of nitrous oxide, and rises to a limit as the concentration of nitrous oxide is increased at a constant concentration of acetaldehyde. In order to keep the walls of the bulb free from carbon during these experiments, air was admitted to the bulb for several minutes after each experiment to burn off the carbon. The air was then pumped out carefully, the bulb flushed with acetaldehyde, and the next experiment made. Representative data are given in Table I. and Fig. 1.

TABLE I.—VARIATION OF THE RATE OF THE REACTION WITH THE PRESSURE OF ACETALDEHYDE AT 480°.

p_{N_2O}	. 102	112	104	103	107	103
p_{CH_3CHO}	. 25	50	100	103	203	332
$t_{\frac{1}{2}}$ (sec.)	. 156	151	158	155	160	155

In spite of the fact that the reaction rate is of the first order with respect to the initial pressure of acetaldehyde, the pressure increase-time curves for individual experiments are more closely represented by an equation with a $3/2$ power of the pressure. The reaction is somewhat retarded by the products, as shown by a small decrease in rate on adding a fresh sample of acetaldehyde to the products of a previous experiment, but the retardation does not seem to be great enough to change the course of the reaction from first order to $3/2$ order, even when the effect of the deposition of carbon on the walls by the reaction is included in the retardation.

The energy of activation of the surface reaction is found to be 26,800 calories per gram molecule.

The Reaction in a "Dirty" Bulb.

The reaction in a bulb of which the walls are covered with carbon is closely $3/2$ order with respect to acetaldehyde as far as 80 per cent. completion, giving a straight line when $[A]^{-1/2}$ is plotted against the time. The

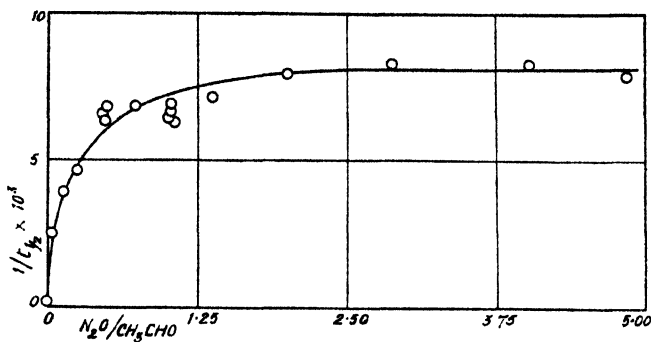


FIG. 1.—Variation of the rate of the reaction with the pressure of nitrous oxide (clean vessel).

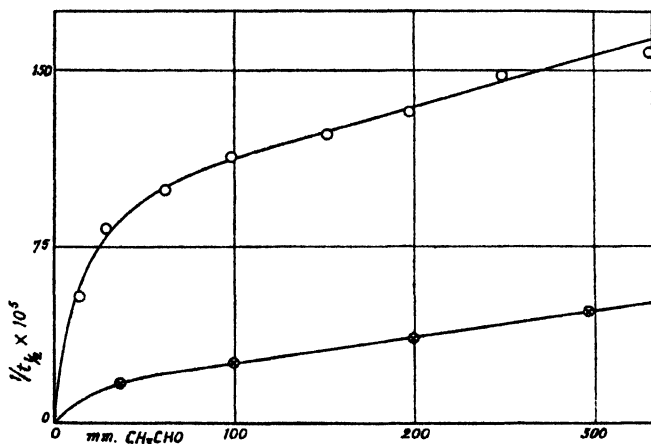


FIG. 2.—Variation of the rate of reaction with the pressure of acetaldehyde in a dirty bulb.

○ Catalysed. ● Uncatalysed.

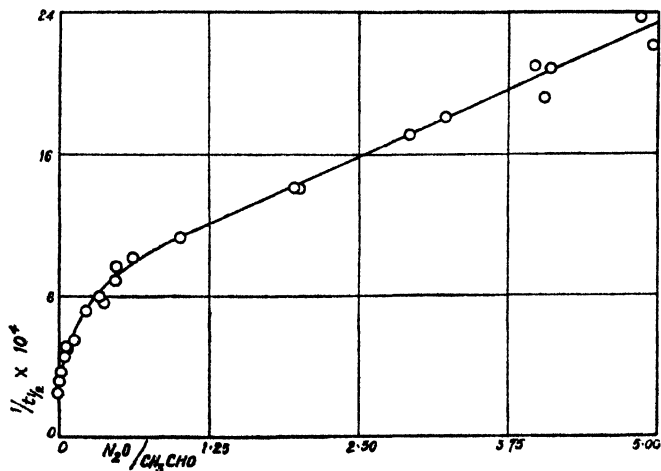


FIG. 3.—Variation of the rate of reaction with the pressure of nitrous oxide in a dirty bulb.

order is independent of the ratio of the concentration of nitrous oxide to the concentration of acetaldehyde and of temperature, as can be demonstrated by plotting a series of affine curves for different experimental conditions. Interpolated data expressing the course of the standard affine curve, which was that for the 100 : 100 mixture, are given in Table II.

TABLE II.—COURSE OF THE REACTION AT 480°.

t (sec.)	110	238	405	608	885	1235	1735	2500
$\Delta p/p_0$	0.10	0.20	0.30	0.40	0.50	0.60	0.70	0.80

The variations of the reaction rate with the pressures of acetaldehyde and nitrous oxide at 480° are shown in Figs. 2 and 3. The lower curve in

TABLE III.—INFLUENCE OF TEMPERATURE ON THE DECOMPOSITION OF ACETALDEHYDE CATALYSED BY NITROUS OXIDE.

Temp. (°Abs.).	p_{N_2O}	p_{CH_3CHO}	$t_{\frac{1}{2}}$ (sec.).
731	100	100	2572
	99	102	2707
753	102	103	1184
	104	102	1215
	100	104	1202
	103	99	1176
770	105	104	639
	106	101	641
	104	103	660
791	108	107	329
	107	108	335

Fig. 2 represents the uncatalysed reaction at the same temperature. It should be noted that the rate is expressed as the reciprocal of the half-life calculated on the basis of the acetaldehyde pressure; the exponent of the acetaldehyde concentration obtained from the curve is therefore less by unity than its exponent in the kinetic equation, while that for nitrous oxide is the same as in the kinetic equation.

On plotting the logarithm of the half-life for the 100 : 100 mixture in the dirty bulb at different temperatures given in Table III. against the reciprocal of the temperature, one obtains a straight line, from the slope of which an energy of activation of 39,800 calories per gram molecule is calculated.

The Decomposition of Acetaldehyde in the Presence of Air.

In order to compare the effect of oxygen on acetaldehyde with the effect of nitrous oxide, a number of observations were made on the decomposition of acetaldehyde in the presence of air. Air was introduced into a capillary pipette at a measured pressure, and then shared to the reaction bulb; 100 mm. of air in the pipette corresponded to 0.48 mm. in the bulb.

The decomposition in the presence of oxygen begins at a high rate, and then drops rather suddenly to a value comparable to the rate of decomposition of acetaldehyde itself. By plotting the rate of reaction at a given percentage decomposition against the percentage decomposition for the oxygen catalysed reaction and for the uncatalysed reaction, and observing the point at which the two curves begin to coincide, the amount of acetaldehyde which decomposes before the effect of the oxygen becomes negligible may be found. This value is greater the greater the excess of acetaldehyde over the amount of oxygen; one volume of oxygen accounts for the decomposition of only 150 volumes of acetaldehyde at 480° when the ratio O_2/CH_3CHO is 3.9×10^{-3} , but for 900 volumes when the ratio is 4.3×10^{-4} . In a bulb packed with silica balls the initial rate is not greatly decreased, but the amount of acetaldehyde decomposed before the oxygen is used up is much less, the pressure increase-time curve bending over at a smaller percentage decomposition. The amount of acetaldehyde decomposed by the oxygen appears again to vary with the ratio of the two constituents.

The initial rate in the unpacked bulb varies linearly with the oxygen

concentration when the pressure is varied between 0.1 mm. and 0.5 mm. with 100 mm. of acetaldehyde. The value for 0.48 mm. air and 100 mm. CH_3CHO at 480° is 0.29 mm. per sec. The variation with the concentration of acetaldehyde is of an order higher than the first.

The decomposition of acetaldehyde in the presence of oxygen has also been studied by Letort,³ using concentrations of oxygen about 1/10 the smallest quantity used here. His results are in general agreement with these. The variation with the oxygen concentration is found to be linear, and a $3/2$ power of the acetaldehyde is found to be involved. For a mixture containing 0.034 mm. O_2 and 226 mm. CH_3CHO at 477° , it was found that one volume of oxygen accounted for the decomposition of 1630 volumes of acetaldehyde.

Summary.

The reaction in the decomposition of acetaldehyde catalysed by nitrous oxide in a clean silica vessel at 480° is first order with respect to acetaldehyde and the rate rises to a limit as the pressure of nitrous oxide is increased. The reaction remaining when the walls of the reaction vessel are covered with carbon is approximately $3/2$ order for a single experiment, and the rate is proportional to the square root of the concentration of nitrous oxide. It is suggested that a reaction between nitrous oxide and acetaldehyde results in the formation of some substance which then acts as a catalyst, or in the initiation of a chain.

The decomposition of acetaldehyde catalysed by oxygen is first order with respect to the oxygen concentration. The amount of acetaldehyde catalytically decomposed by a given quantity of oxygen is greater the greater the excess of acetaldehyde.

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³ Letort, *Compt. rend.*, 1933, **197**, 1042; 1935, **200**, 312.

THE DECOMPOSITION OF ACETALDEHYDE CATALYSED BY NITRIC OXIDE.

By F. H. VERHOEK.

(Communicated by C. N. HINSHELWOOD.)

Received 22nd July, 1935.

In order to obtain data which might be useful in the interpretation of the results of the study of the decomposition of acetaldehyde catalysed by nitrous oxide, its catalysis by nitric oxide was investigated. The latter reaction is simpler than the former in that it does not show a surface reaction, but it is complicated by the superposition of two effects, one an induced catalysis initiated by an oxidation, and the other a simple collisional catalysis as with nitric oxide and chloral. The reaction was studied at 480° . The pressure increase-time curves are again found to be approximately $3/2$ order with respect to acetaldehyde, and the low-pressure portions of the curves for the variation of the reaction rate with the initial pressures of the reactants are similar to those with nitrous oxide. Either of the mechanisms proposed for nitrous oxide and acetaldehyde, therefore, will serve here. At high pressures of nitric

oxide, however, the rate becomes directly proportional to the pressure of nitric oxide. This seems to be explained only by assuming that nitric oxide exerts a direct catalysis on acetaldehyde on collision with it.

The apparatus and the preparation of the materials have been described in the two preceding papers.

End-point and Products.

The total pressure increase is 97 per cent. of the initial pressure of acetaldehyde. The averaged results of four analyses of the reaction products at the end-point showed 3 per cent. less of nitric oxide and methane than the values calculated from the initial concentrations of the constituents and for the decomposition products of the uncatalysed reaction respectively, and increase of 1 per cent. in the amount of carbon monoxide produced, and 2 per cent. residue. That these results indicate an oxidation by such a stable molecule as nitric oxide seemed at first unlikely, but this view is supported by the results of an attempt to study the catalytic decomposition of acetone by nitric oxide at the higher temperature 600°. Here the reaction was found to be predominantly an oxidation, with a disappearance of methane and the formation of an excess of carbon monoxide and carbon dioxide, as compared with the products of the decomposition of acetone at the same temperature. With acetaldehyde and nitric oxide the presence or absence of a small quantity of carbon dioxide was uncertain because of the solubility of nitric oxide in the absorbents. A test of the products with baryta was negative. It has been reported that the catalytic oxidation of hydrocarbons by nitric oxide at 500° C. forms ammonia.¹ No ammonia could be detected in the products.

Effect of Surface and Course of Reaction.

The reaction goes somewhat more rapidly when the walls of the reaction bulb are covered with carbon than when they are clean. The effect of the wall is thus opposite to the effect with nitrous oxide and acetaldehyde. The progressive deposition of carbon in successive reactions is again observed, as well as the return to the original rate on burning off the carbon.

The retarding effect of the walls is likewise observed in a bulb packed with silica balls, for which the rate when clean was less than one-quarter of that in the dirty unpacked bulb. On covering the surface in the packed bulb with carbon, however, the rate increased nearly to the value in the clean unpacked bulb.

At 480° the course of a single reaction in the unpacked bulb is expressed by an equation involving a 3/2 power of the acetaldehyde concentration. The course of the reaction is not changed by changing the partial pressures of the two components of the reaction mixture. At lower temperatures, however, an initial acceleration appears, which becomes quite noticeable at the lowest temperature for which the rate of reaction was observed (447°), where the point of inflection in the pressure increase-time curve occurs at about 1/2 of the half-time and 8 per cent. completion. At 480°, where most of the experiments were made, the initial acceleration is barely detectable, and may be neglected in considering the rate data.

The data for a typical experiment at 480° are given in Table I.

TABLE I.—COURSE OF REACTION AT 480°.

CH₃CHO = 102 mm.; NO = 101 mm.; t₁ = 399 sec.

Time (sec.) .	34	68	101	135	199	250	321	376
$\Delta p/p_0 \times 100$	2.0	5.9	10.8	16.7	28.4	35.3	43.1	48.0
Time (sec.) .	433	535	694	1037	1485	1890	2460	
$\Delta p/p_0 \times 100$	52.9	59.8	67.8	76.2	84.1	89.1	90.1	

¹ Platonov and Schaikind, *J. Gen. Chem. Russ.*, 1934, 4, 434.

Order of Reaction.

The variation of the reaction rate with the pressure of nitric oxide at 100 mm. of acetaldehyde at 480° is shown in Fig. 1, where the reciprocal

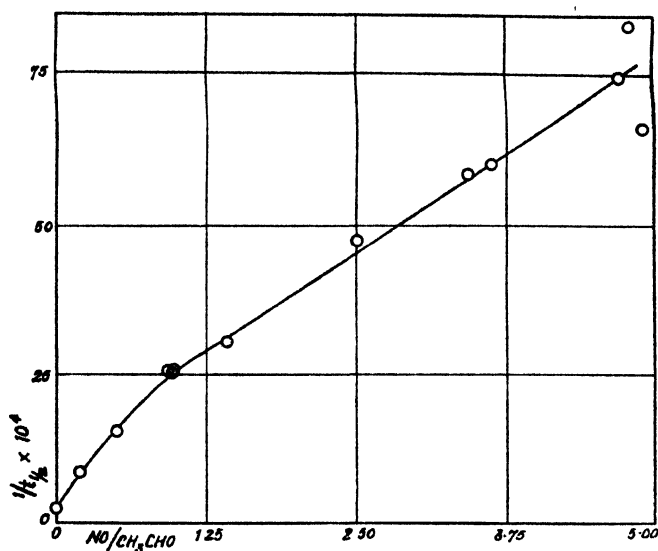


FIG. 1.—Variation of the rate of reaction with the pressure of nitric oxide.

of the time for half change is plotted against the ratio $\text{NO}/\text{CH}_3\text{CHO}$. The rate becomes proportional to the nitric oxide concentration when the nitric oxide is in excess.

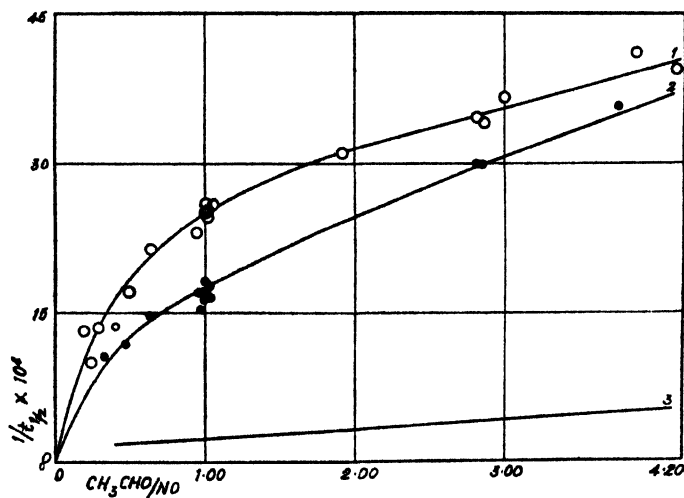


FIG. 2.—Variation of the rate of reaction with the pressure of acetaldehyde.
1. Dirty bulb. 2. Clean bulb. 3. Uncatalysed.

The rate varies with the concentration of acetaldehyde at 100 mm. NO at 480° in the manner shown in Fig. 2. The top curve in this figure represents the reaction in a bulb with the walls covered with carbon, the

middle curve represents the reaction in a clean bulb, and the lowest curve is for the uncatalysed reaction. The rate in the clean bulb is approaching that in the dirty bulb as the pressure increases. This is to be expected, since the retarding effect of the wall must depend upon the ease with which the gases reach the wall, so that wall effects become less marked at higher pressures.

Temperature Coefficient.

The data for determining the energy of activation are given in Table II. The value found for E is 37,300 calories per gram molecule.

TABLE II.—TEMPERATURE COEFFICIENT OF THE NITRIC OXIDE-ACETALDEHYDE REACTION.

Temp. (°Abs.).	p_{NO} .	$p_{\text{CH}_3\text{CHO}}$.	$t_{\frac{1}{2}}$ (sec.).
720	96	97	1295
	95	99	1258
740	96	96	642
	96	97	648
753	99	101	365
	101	96	423
	101	96	395
	97	105	420
	94	101	422
779	104	106	172
	100	106	189
	99	107	183

The author wishes to express his thanks to Mr. C. N. Hinshelwood for his help and criticism during the course of the investigations described in this paper and the two preceding papers.

Summary.

The decomposition of acetaldehyde catalysed by nitric oxide at 480° is roughly 3/2 order with respect to acetaldehyde, and the rate becomes proportional to the concentration of nitric oxide when the nitric oxide is in excess. At lower temperatures an initial ac-

celeration occurs. The rate of reaction is decreased by an increase in the surface to volume ratio in clean silica vessels, but is not greatly affected by such a change if the silica walls are covered with carbon. It is suggested that the catalysis is the result of the combination of two effects, one like that found for nitric oxide and chloral, and one like that for nitrous oxide and acetaldehyde.

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THE STERIC FACTOR OF BIMOLECULAR ASSOCIATION REACTIONS.

BY C. E. H. BAWN.

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According to the kinetic theory, the velocity constant of a bimolecular reaction can be satisfactorily represented by an expression of the type $k = pZe^{-E/RT}$, where E is the activation energy, Z the number of collisions between the two reacting molecules, and p a steric factor which takes account of the fact that not all collisions between molecules with the required energy lead to reaction. The value of p which is normally of the order 1 to 10^{-1} , may, in certain types of reaction, have values of

the order of 10^{-4} to 10^{-8} . Reactions belonging to the latter classes include association reactions between complex molecules or radicals, such as the gaseous bimolecular polymerisation of ethylene¹ and a group of bimolecular reactions in solution, for example, the reaction in which tertiary nitrogen compounds combine with alkyl halides with the formation of quaternary compounds, ("Slow reactions").²

The object of this paper is to develop further the views as to the "slowness" of these reactions. On account of the greater simplicity of the treatment, the work is confined to gaseous reactions, it is to be expected that the same principles will hold true for reactions in solution.

It is shown that the magnitude of the steric factor is primarily determined by the complexity of the reacting molecules. Association reactions between molecules possessing large numbers of degrees of freedom will have small steric factors, whereas when one or more of the reacting partners is an atom, the value of p will tend to the normal value of unity.*

Steric Factor and Reaction Velocity.

Recently, several new attempts have been made to calculate the absolute rate of chemical reaction by the method of the transition state. The application of this method with special reference to potential energy surfaces was first made by Peltzer and Wigner³ in the case of the reaction of a hydrogen atom with a hydrogen molecule. Recently, a generalisation of their treatment has been independently given by Eyring⁴ and by Evans and Polanyi.⁵ The basis of both of these latter methods is that the reaction consists in the passage of the reacting system over an energy barrier from the initial to the final state—the height of the "saddle point" (transition state) determining the activation energy. This energy surface may be calculated by the method of Eyring and Polanyi,⁶ whilst the motion of the system over the surface (except in special cases) may be determined in terms of the kinetic theory. As an illustration of the method we shall consider the simple formulation of Evans and Polanyi.

It is assumed that every time a representative point passes across the transition layer (which is defined in terms of the co-ordinate of the reaction path) the completion of chemical reaction in that direction occurs. By a consideration of the equilibrium between the initial and the final state the reaction velocity is calculated in terms of the probability of the transition state, and the time required for the representative to pass through the transition state in the direction of reaction.

It is shown that the reaction velocity may be represented by

$$\begin{aligned}\text{Reaction velocity} &= \frac{1}{2} \frac{\text{Probability of Transition State}}{\text{Life Time}} \\ &= \frac{1}{2} P v,\end{aligned}$$

¹ Pease, *J.A.C.S.*, 1932, **54**, 1876.

² Moelwyn-Hughes and Hinshelwood, *J. Chem. Soc.*, 1932, 230. See also Moelwyn-Hughes, *Kinetics of Reactions in Solution*, Oxford, 1933.

³ Peltzer and Wigner, *Z. physik. Chem. B.*, 1932, **15**, 445.

⁴ Eyring, *J. Chem. Physics*, 1935, **3**, 107.

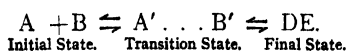
⁵ Evans and Polanyi, *Trans. Faraday Soc.*, 1935, **31**, 875.

⁶ Eyring and Polanyi, *Z. physikal. Chem., B.*, 1931, **12**, 279.

* A similar conclusion has been reached by Hinshelwood and his co-workers for reactions in solution. (See Hinshelwood and Legard, *J. Chem. Soc.*, 1935, p. 595.) They conclude that when one of the reacting species is an ion, p approaches unity very closely.

where P is the probability of the transition state, and v is the average velocity of the representative point along the translation degree of freedom corresponding to decomposition. The above expression reduces to $k = \frac{1}{2}Kv$ where K is the equilibrium constant between the initial and the transition state. Now both K and v can be calculated^{4, 5, 7} by use of the methods stated, and the expression so obtained gives the rates in terms of the probability of the transition state. The latter factor now replaces the collision factor of the kinetic theory of reaction velocity. A closer consideration of the probability factor leads directly, as pointed out by Evans and Polanyi⁶ to an interpretation of the small steric factor found in the rates of association reactions between complex molecules. This will be made clear by means of a simple example:

Consider the reaction



The equilibrium constant K between the initial and the transition state may be calculated in terms of the partition functions (f), (see p. 1542) of the molecules A and B and $A' \dots B'$. In the general case when A and B are complex molecules

$$K = \frac{f_{A'B'} e^{-E/kT}}{f_A f_B} = \frac{\left(\frac{2\pi(m_1 + m_2)kT}{h^2}\right)^{\frac{3}{2}} V 8\pi^2 \cdot \frac{(8\pi^3 A_1 A_2 A_3)^{\frac{1}{2}} (kT)^{\frac{3}{2}}}{\sigma_1 h^3} \cdot \Pi_i \left(1 - \exp\left(-\frac{h\nu}{kT}\right)\right)^{-1}}{\left(\frac{2\pi m_1 kT}{h^2}\right)^{\frac{3}{2}} V \cdot \left(\frac{2\pi m_2 kT}{h^2}\right)^{\frac{3}{2}} V \cdot \frac{8\pi^2 (8\pi^3 A'_1 A'_2 A'_3)^{\frac{1}{2}} (kT)^{\frac{3}{2}}}{\sigma_2 h^3} \cdot \frac{8\pi^2 (8\pi^3 A''_1 A''_2 A''_3)^{\frac{1}{2}} (kT)^{\frac{3}{2}}}{\sigma_3 h^3} \cdot \frac{\Pi_i \Pi_k \left(1 - \exp\left(-\frac{h\nu}{kT}\right)\right)^{-1} \times \frac{(2\pi m^* kT)^{\frac{1}{2}}}{h} \cdot e^{-E/kT}}{1}}$$

the last term in the expression $\frac{(2\pi m^* kT)^{\frac{1}{2}}}{h}$ is the translational partition function corresponding to the motion of the system along the reaction co-ordinate l , m^* being the reduced mass of the reacting system. If A and B are atoms, then K_a is equal to

$$K_a = \frac{\left(\frac{2\pi(m'_1 + m'_2)kT}{h^2}\right)^{\frac{3}{2}} V \cdot \frac{8\pi^2 I kT}{\sigma h^2} \cdot \left(1 - \exp\left(-\frac{h\nu}{kT}\right)\right)^{-1}}{\left(\frac{2\pi m'_1 kT}{h^2}\right)^{\frac{3}{2}} V \cdot \left(\frac{2\pi m'_2 kT}{h^2}\right)^{\frac{3}{2}} V} \times \frac{(2\pi m^{**} kT)^{\frac{1}{2}}}{h} \cdot e^{-E_a/kT}.$$

The importance of this probability factor in relation to the reaction velocity can be seen directly by comparing the probabilities of the collided state in the above cases involving complex molecules and atoms respectively. If the masses are assumed respectively equal, i.e., $m_1 = m'_1$, $m_2 = m'_2$ and that we omit all energy considerations since we are only interested at the present in the probability factor independent of energy; then

⁷ See also Kassel, *J. Chem. Physics*, 1935, 3, 1935.

$$\frac{K}{K_a} = \left(\frac{A_1 A_2 A_3}{A_1' A_2' A_3' A_1'' A_2'' A_3''} \right)^{\frac{1}{2}} \frac{1}{I} \frac{\sigma \sigma_2 \sigma_3}{\sigma_1} \frac{h^5}{(8\pi^2)^2 (8\pi^3)^{\frac{1}{2}}} \cdot \frac{1}{(kT)^{\frac{3}{2}}} \frac{\prod_{i=1}^{i=5} \left(1 - \exp\left(-\frac{h\nu_i}{kT}\right) \right)^{-1}}{\left(1 - \exp\left(-\frac{h\nu_1}{kT}\right) \right)^{-1}} \cdot \left(\frac{m^*}{m^{**}} \right)^{\frac{1}{2}}.$$

An approximate value of this ratio can be obtained taking all moments of inertia as 10^{-39} C.G.S., all σ 's = 1 and $\left(1 - \left(\exp - \frac{h\nu}{kT} \right) \right)^{-1} \approx \frac{kT}{h\nu} \approx 1$ then at 300° K

$$\frac{K}{K_a} = 10^{-6} \cdot \left(\frac{m^*}{m^{**}} \right)^{\frac{1}{2}}$$

since the relative rate of reaction $\frac{k_1}{k_2} = \frac{K}{K_a} \cdot \frac{v_1}{v_2}$ it follows that

$$\frac{k_1}{k_2} = \frac{K}{K_a} \cdot \frac{\frac{kT}{(2\pi m^* kT)^{\frac{1}{2}}}}{\frac{kT}{(2\pi m^{**} kT)^{\frac{1}{2}}}} = \frac{K}{K_a} \cdot \left(\frac{m^{**}}{m^*} \right)^{\frac{1}{2}} \approx 10^{-6}.$$

It is at once apparent that the relative slowness of reaction between complex molecules is due to the decreased probability of the collided state in reaction between such molecules. This will appear in the reaction velocity expression as a steric factor. A similar conclusion has been previously reached by Evans and Polanyi⁵ for bimolecular reactions in solution ("Slow Reactions").

Steric Factor and Equilibrium Constant.

This reduced probability of the collided state will also appear in the equilibrium constant between the initial and the final state if it is assumed that the configuration of the transition state is similar to that of the final state. Polanyi and Wigner⁶ have employed this assumption in deducing the formula $k_{\text{uni}} = \nu e^{-E/RT}$. We may use the formulation of this paper to arrive at a similar result as the following calculation shows:

The equilibrium constant K between the final and transition states given by

⁵ An equation of this form was first deduced by Herzfeld (*Ann. Physik*, 1919, 59, 635), (see also Muller-Pouillet, *Lehrbuch der Physik. Kinetische Theorie der Wärme*, p. 199, 1925), for the dissociation of a diatomic molecule under conditions in which every collision of free atoms would lead to the formation of a molecule. It has also been claimed as an empirical rule applicable to monomolecular reactions in general by Dushman (*J.A.C.S.*, 1921, 43, 397). Rodebush (*J.A.C.S.*, 1923, 45, 606), has pointed out that the equation could be explained on the assumption that a bond having an excess of energy would lose it in a time $1/\nu$. Dealing with the problem of condensation, Baule (*Ann. Physik*, 1914, 44, 195), showed that the condensation energy of an atom is used at every collision with a solid surface.

$$K = e^{-E_a/kT} \frac{\left(\frac{8\pi^3 A_1 A_2 A_3}{\sigma_1 h^3} \right)^{\frac{1}{2}} \prod_{i=1}^{i=3n-7} \frac{kT}{h\nu_i}}{\left(\frac{8\pi^3 A'_1 A'_2 A'_3}{\sigma_1 h^3} \right)^{\frac{1}{2}} \prod_{i=1}^{i=3n-6} \frac{kT}{h\nu_i}} \times \frac{(2\pi m^* kT)^{\frac{1}{2}}}{h}$$

$$\approx e^{-E_a/kT} \left(\frac{A_1 A_2 A_3}{A'_1 A'_2 A'_3} \right)^{\frac{1}{2}} \frac{\prod_{i=1}^{i=3n-7} \frac{kT}{h\nu_i}}{\prod_{i=1}^{i=3n-6} \frac{kT}{h\nu_i}} \frac{(2\pi m^* kT)^{\frac{1}{2}}}{h}$$

which when multiplied by the associated velocity⁴ $\frac{kT}{(2\pi m^* kT)^{\frac{1}{2}}}$ gives the unimolecular reaction velocity constant

$$k_{\text{uni}} = e^{-E_a/kT} \left(\frac{A_1 A_2 A_3}{A'_1 A'_2 A'_3} \right)^{\frac{1}{2}} \frac{\prod_{i=1}^{i=3n-7} \frac{kT}{h\nu_i}}{\prod_{i=1}^{i=3n-6} \frac{kT}{h\nu_i}} \cdot \frac{kT}{h}.$$

which reduces to

$$k_{\text{uni}} = e^{-E_a/kT} \left(\frac{A_1 A_2 A_3}{A'_1 A'_2 A'_3} \right)^{\frac{1}{2}} \cdot \frac{h\nu}{kT} \cdot \frac{kT}{h} \approx \nu e^{-E_a/kT}.$$

This shows that the assumption of a normal unimolecular results in the full force of the steric factor of the association reaction making its appearance in ordinary equilibrium constant between the initial and final states.

The effect of the complexity of the molecule may now be quite clearly seen by comparing the equilibrium constant of the bimolecular association of molecules with a large number of degrees of freedom, with similar reactions between atoms or molecules with the same mass. In the examples given in the following table the equilibrium constants

Temp.	Complex Molecules.		Simple Molecules	
	Reaction.	Equilibrium Const.	Reaction	Equilibrium Const.
1500	$\text{C}_3\text{H}_8 \rightleftharpoons \text{C}_2\text{H}_6 + \text{CH}_4$	$\log_{10} K = 9.53 - \frac{80,000}{2.3RT}$	$\text{SO} \rightleftharpoons \text{S} + \text{O}^9$	$\log_{10} K = 5.71 - \frac{116,500}{2.3RT}$
1500	$\text{C}_3\text{H}_8 \rightleftharpoons \text{C}_2\text{H}_6 + \text{CH}_4$	$\log_{10} K = 9.45 - \frac{80,000}{2.3RT}$	$\text{O}_2 \rightleftharpoons \text{O} + \text{O}^{10}$	$\log_{10} K = 6.28 - \frac{117,300}{2.3RT}$
600	$\text{C}_2\text{H}_6 \rightleftharpoons \text{C}_2\text{H}_4 + \text{H}_2$	$\log_{10} K = 6.31 - \frac{31,244}{2.3RT}$	$\text{H}_2\text{S} \rightleftharpoons \text{H}_2 + \text{S}^{11}$	$\log_{10} K = 4.55 - \frac{71,270}{2.3RT}$

^{9, 10, 11} These values are determined from the calculations of the following workers:

Zeise, *Z. Electrochemie*, 1934, 40, 885 (Review).

Montgomery and Kassel, *J. Chem. Physics*, 1934, 2, 418.

Johnson and Walker, *J.A.C.S.*, 1933, 55, 172, 187.

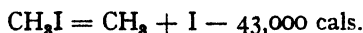
Cross, *J. Chem. Physics*, 1935, 3, 168.

have been calculated from the observed molecular properties (Moments of Inertia, Frequencies, etc., see page 1542). It is evident that the associated state is much more probable in the reactions of simple molecules.

Data on Steric Factor : Calculated and Observed.

From a knowledge of the equilibrium constant we have been able to evaluate the steric factor for a number of association reactions.* The method of procedure was as follows :—

The equilibrium constant K was calculated from the partition function of the molecules in the initial and the final states. Now $K = \frac{k_{\text{uni}}}{k_{\text{bi}}}$ and, therefore, by taking the experimentally determined or otherwise appropriate values for k_{uni} , k_{bi} could be evaluated. But $k_{\text{bi}} = pZe^{-E/RT}$ and hence, from known values of Z and E and comparison of k_{bi} thus obtained in terms of p with that calculated from the equilibrium constant we obtain directly the value of p . The following example will serve to illustrate the method : the decomposition of methyl iodide



as shown by Ogg¹²

$$k_{\text{uni}} = 3.93 \times 10^{12} e^{-\frac{43,000}{RT}} \text{ sec.}^{-1}$$

at 600° abs.

$$k_{\text{bi}} = 10.57 \times 10^{-4} \text{ sec.}^{-1}$$

The calculated equilibrium const. at 600° = 1.9×10^{-14} atm.

$$\therefore k_{\text{bi}} = \frac{k_{\text{uni}}}{K} = 1.2 \times 10^{15} \text{ c.c. mole}^{-1} \text{ sec.}^{-1}$$

assuming the reverse reaction requires no activation energy

then

$$k_{\text{bi}} = pZ \approx p10^{14} \text{ c.c. mole}^{-1} \text{ sec.}^{-1}$$

and hence by comparison the steric factor $p \approx 1$.

A more straightforward means of evaluating p obtains when the dependence of the equilibrium constant on temperature is known. This is usually written in conformity with the third law of thermodynamics in the form

$$\ln K = \frac{Q}{RT} + f(T) + C \quad . \quad . \quad . \quad (1)$$

¹² Ogg, *J. Amer. Chem. Soc.*, 1934, **56**, 527.

* It has been shown by Rodebush (*J. Chem. Physics*, 1933, **1**, 440), and more recently by Rice and Gershinowitz (*ibid.*, 1934, **2**, 853) that considerable information about the kinetics of a reaction may be obtained from the statistical expression for the equilibrium constant. The equilibrium constant may be expressed in the form

$$-\log K = \frac{\Delta H}{RT} - \frac{\Delta S}{R}$$

If ΔH and ΔS could be divided in the correct way the values of k_1 and k_2 could be determined. The division of ΔH is known, and the paper of Rice and Gershinowitz is concerned with the division of ΔS . By making assumptions relating to the change of the degrees of freedom which occur on reaction they arrive at an interpretation of the collision number and the steric factor of a reaction. Their treatment, requires a special knowledge of the mechanism of the reaction for each case. In the present case we employ the relationship $k_{\text{uni}} = \nu e^{-E/RT}$ in dividing the equilibrium constant.

where $C = \text{constant}$,

but
$$K = \frac{k_{\text{uni}}}{k_{\text{bi}}} = \frac{A_1 e^{-E_1/RT}}{pZ e^{-E_2/RT}} = \frac{A_1}{pZ} \cdot e^{Q/RT}$$

where $Q = \text{heat of reaction}$

and thus
$$\ln K = \frac{Q}{RT} + \ln \frac{A_1}{pZ} \quad (2)$$

TABLE 1a.

Reaction.	Temp. °K.	Equilibrium Constant (Atm.).	$k_{\text{uni}} \text{ sec.}^{-1}$	Activation Energy.		$k_{\text{bi}} \text{ (cal.) c. mol.}^{-1} \text{ sec.}^{-1}$	$k_{\text{bi}} = pZ e^{-E/RT}$	p .
				uni.	bi.			
$\text{N}_2\text{O} \rightarrow \text{N}_2 + \text{O}$	1000	$5.72 \cdot 10^{-6} a$	$2.92 \cdot 10^{-2} b$	53,000	11,500	$1.14 \cdot 10^6$	$3.93 \cdot 10^{-3} pZ^*$	$3 \cdot 10^{-4} c$
$\text{CH}_3\text{I} \rightarrow \text{CH}_3 + \text{I}$	600	$1.9 \cdot 10^{-14}$	$10.57 \cdot 10^{-4} d$	43,000	0	$1.2 \cdot 10^{15}$	pZ	≈ 1
$\text{CH}_3 \cdot \text{CH}_3 \rightarrow 2\text{CH}_3$	1500	$7.43 \cdot 10^{-8}$	$2.64 \cdot 10^{-12}$	80,000 ^e	0	$7.97 \cdot 10^8$	pZ	$8 \cdot 10^{-6}$
			$7.38 \cdot 10^{-11}$	70,000	0	$2.24 \cdot 10^{10}$	pZ	$2 \cdot 10^{-6}$
			$2.64 \cdot 10^{-12}$	80,000	8,000	$7.97 \cdot 10^8$	$7 \cdot 10^{-3} pZ$	10^{-4}
$\text{C}_2\text{H}_5 \cdot \text{CH}_3 \rightarrow \text{C}_2\text{H}_5 + \text{CH}_3$	1500	$9.0 \cdot 10^{-8}$	$2.64 \cdot 10^{-12}$	80,000	0	$6.57 \cdot 10^7$	pZ	$7 \cdot 10^{-5}$
				80,000	8,000	$6.57 \cdot 10^7$	$7 \cdot 10^{-3} pZ$	10^{-5}
$\text{CH}_3\text{COCH}_3 \rightarrow \text{CH}_3\text{CO} + \text{CH}_3$	800	$2.75 \cdot 10^{-11}$	$1 \cdot 10^{-5}$	70,000	0	$8 \cdot 15 \cdot 10^8$	pZ	$8 \cdot 10^{-6}$

* In calculating p by comparison of the results of columns 7 and 8, Z in all cases was taken as 10^{14} c.c. mole.⁻¹ sec.⁻¹.

^a Calculated from free energy values of N_2O , N_2 and O as given by

Kassel, *J.A.C.S.*, 1935, **58**, 1838.

Johnson and Davis, *ibid.*, 1934, **56**, 271.

Johnson and Walker, *ibid.*, 1933, **55**, 172.

^b Kassel, *Kinetics of Homogeneous Gas Reactions*, Chem. Catalogue Co., p. 227.

^c The appearance of large steric factors in certain reactions of the association of atoms and simple molecules, e.g., $\text{N}_2 + \text{O} \rightarrow \text{N}_2\text{O}$ cannot be ascribed to the reduced probability of the collided state in the sense we have considered it. The effect has been interpreted in the literature (Hertzberg, *Z. physikal. Chem. B.*, 1932, **17**, 68; Peltzer and Wigner, *ibid.*, *B.*, 1932, **15**, 445) as arising from the fact that the transition state is formed by the crossing of the potential curves representing the two states of the system involved in the reaction. Such steric factors will appear both in the forward and reverse reactions and thus will not be included in the equilibrium constant.

^d Ogg, *loc. cit.*¹²

^e For the decomposition of the hydrocarbons the activation energy of the unimolecular dissociation was taken both as 70,000 and 80,000 cal. (the C—C bond energy is most probably 77-78 cal.). It is also assumed that the reverse reaction requires an activation energy of either zero or 8,000 cal. It is seen from the table that this produces a variation of p of 10^{-4} — 10^{-6} . The unimolecular decomposition was calculated from $k = A e^{-E/RT}$ A being taken as 10^{12} sec.⁻¹ where no experimental value was available.

^f Association reactions between single atoms with the formation of diatomic molecules have not been included in the above table, since it is well known that these reactions require the presence of a third body to remove the energy of the bond formed. It should also be observed as shown by Kassel (*J. Amer. Chem. Soc.*, 1931, **53**, 2143) that no such restriction is necessary for the association of complex molecules or radicals.

Calculation of Equilibrium Constants.

As previously stated, the equilibrium constant of the association reaction

$\text{A} + \text{B} \rightleftharpoons \text{C}$ may be written $K = \frac{f_0}{f_A f_B} \cdot e^{-E/RT}$, where f_A , f_B , f_0 are the complete partition functions of A, B and C respectively, and E is the difference in energy

TABLE 1b.

Reaction.	Equilibrium Const. (Atm.).	$\frac{A_1}{pZ}$ c.c. mol. ⁻¹ sec. ⁻¹ .	$p \left(\frac{A_1}{Z_1} \approx 10^{-1} \right)$.
$N_2O_4 \rightleftharpoons 2NO_2$	$\log_{10} K_P = -\frac{13,600}{2.3RT} + 9.0$	$5 \cdot 10^4$	2×10^{-6}
$HCHO \rightarrow H_2 + CO^a$	$\log_{10} K_P = -\frac{11,800}{4.57T} + 1.75 \log T + 0.0001 T + 0.3$	4×10^6 (600° K.)	2.5×10^{-7} *
$C_2H_4 \rightarrow H_2 + C_2H_2^b$	$\log_{10} K_P = -\frac{49,200}{2.3RT} + 7.54$	$1.5 \cdot 10^3$	6.6×10^{-4}
$C_2H_4 \rightarrow C_2H_2 + H_2^c$	$\log_{10} K_P = -\frac{31,244}{2.3RT} + 6.31$	9×10^3	1.2×10^{-4}
$C_2H_4 + H_2O \rightarrow C_2H_5OH^d$	$\log_{10} K_P = -\frac{9600}{2.3RT} - 6.195$	7×10^3	1.4×10^{-4}
$CH_2 \cdot CH_2 = CH_2 + H_2O \rightarrow C_2H_5O^e$	$\log_{10} K_P = -\frac{8970}{2.3RT} - 6.060$	8×10^3	1.25×10^{-4}
$(CH_3)_2C=CH_2 + H_2O \rightarrow (CH_3)_2C(OH)^f$	$\log_{10} K_P = -\frac{9000}{2.3RT} - 6.060$	5×10^3	2×10^{-4}
$CH_2 \cdot CH = CH \cdot CH_3 + H_2O \rightarrow^g$	$\log_{10} K_P = -\frac{8487}{2.3RT} - 6.395$	1×10^4	1×10^{-3}
$C_2H_5Br \rightarrow C_2H_6 + HBr^h$	$\log_{10} K_P = -\frac{17,000}{2.3RT} + 7.17$	7×10^4	1.4×10^{-5}
$C_2H_4I_2 \rightarrow C_2H_4 + I_2^i$	$K_P = 1.1$ at 343° K.	$\Delta H = -7600$ cals. ^j $E_{uni} = 36,600^k$	$p \approx 10^{-2}$

^a Ghosh and Chakravarty, *Quart. J. Indian Chem. Soc.*, 1925, **2**, 142.

^b Park and Huffman, *Free Energies of Organic Compounds*, Chem. Catal. Co., p. 105.

^c Pease, *J.A.C.S.*, 1932, **54**, 1876.

^d, ^e, ^f, ^g Stanley, Yowell and Dymock, *J. Soc. Chem. Ind.*, 1934, **53**, 206T.

^h Brunel, *J.A.C.S.*, 1917, **39**, 1978.

ⁱ Mooney and Ludlam, *Proc. Roy. Soc. Edin.*, 1929, **48**, 160.

^j Sherman and Sun, *J.A.C.S.*, 1924, **56**, 1098.

^k Arnold and Kistiakowsky, *J. Chem. Physics*, 1933, **1**, 166.

* This reaction is known to proceed via the crossing of two energy surfaces (predissociation mechanism).

between the initial and the final states. The partition function will take the form $f = f_T f_R f_V$ where f_T , f_R , f_V are the partition functions for translation, rotation and vibration respectively. (It is assumed that the temperature is high enough for the rotational states to be fully excited.) The general form of f for a polyatomic molecule will be

$$f = \left(\frac{2\pi m kT}{h^2} \right)^{\frac{3}{2}} V \cdot 8\pi^2 \frac{(8\pi^2 A_1 A_2 A_3)}{\sigma h^3} (kT)^{\frac{3}{2}} \cdot \prod_i (1 - e^{-h\nu_i/RT})^{-1}$$

where m is the mass of the molecule, A_1 , A_2 , A_3 are the moments of inertia; σ the symmetry number and ν the frequency of vibration. If $h\nu_i \ll kT$ the vibrational partition function reduces to $\prod_i \frac{kT}{h\nu_i}$ the form generally used in our calculations.

In some cases K was calculated from the entropy by use of the relationship $-RT \ln K = H - T\Delta S$ where H heat of reaction and ΔS the entropy change.

* This expression needs modification when the molecule possesses internal rotations (see following paragraph).

TABLE Ic.

Reaction.	k (theoretical) litre Mole. ⁻¹ Sec. ⁻¹ .	k (expt.) (Temp. °K.)	p .
$H_2 + C_2H_4 \rightarrow C_2H_6^a$	2.46 ($E = 35,700$)	0.0114 (698)	4.5×10^{-3}
$2C_2H_4 \rightarrow C_4H_8^b$	0.589	0.00159 (773)	2.7×10^{-3}
$2CH_2=CH-CH_2=CH_2 \rightarrow C_4H_8^c$	273.0	0.0265 (614)	1×10^{-4}
$2CH_2-\overset{\text{CH}_3}{\underset{\text{CH=CH}_2}{\text{C}}} \rightarrow C_{10}H_{18}^d$	2.21	0.00415 (570)	1.9×10^{-5}
	<i>B</i>	<i>E</i>	<i>p</i>
$2C_2H_4 \rightarrow C_4H_8^e$	10.85	38,400	4×10^{-3}
$2CH_2 \cdot CH=CH_2 \rightarrow C_4H_8$	10.2	38,000	1×10^{-3}
$2CH_2 \cdot CH=CH \cdot CH \rightarrow C_6H_{10}$	10.0	38,000	5×10^{-4}
Amylene (of unknown composition)	9.8	38,000	$4 \cdot 10^{-4}$
$2CH_2-\overset{\text{CH}_3}{\underset{\text{CH}_3}{\text{C}}}-CH_2 \rightarrow C_6H_{10}$	12.3	43,000	1×10^{-1}

^a Pease, *J.A.C.S.*, 1932, **54**, 1876.^b Pease, *ibid.*, 1930, **52**, 1138; *ibid.*, 1931, **53**, 613.^c Vaughan, W. E., *J.A.C.S.*, 1932, **54**, 3863.^d *ibid.*, 1933, **55**, 4108.^e Krautz, Nemtsov and Sovking, *Compt. Rend., Acad. Sci. U.R.S.S.*, 1934, **3**, 265. The results of these workers are expressed in the form

$$\log k = B - E/RT,$$

where k is in the units litre Mole.⁻¹ Sec.⁻¹. p was evaluated by comparing B with the theoretical collision number $Z = 2N^2\sigma^2 \sqrt{\frac{\pi kT}{m}}$,where N = no. of molecules per c.c. and σ the collision diameter which was taken as 4×10^{-8} cm.Using the same rotation, the entropy of a diatomic and non-linear polyatomic molecule¹² may be written:

$$S_{\text{diatomic}} = R \left[\ln \frac{V}{N} \cdot \left(\frac{2\pi mkT}{h^2} \right)^{\frac{3}{2}} \cdot e^{\frac{5}{2}} \cdot \left(\frac{8\pi^2 I kT}{h^2} \right) e p_e p_n + \frac{h\nu/kT}{e^{h\nu/kT} - 1} - \ln \left(1 - e^{-h\nu/kT} \right) \right]$$

$$S_{\text{polyatomic}} = R \left[\ln \frac{V}{N} \left(\frac{2\pi mkT}{h^2} \right)^{\frac{3}{2}} e^{\frac{5}{2}} \cdot \left(\frac{8\pi^2 (A_1 A_2 A_3)^{\frac{1}{2}} kT}{h^2} \right)^{\frac{3}{2}} e^{\frac{3}{2}} p_e p_n \frac{1}{\sigma} + \sum_{i=1}^{i=3n-6} S_{\text{Eln.}}(\nu_i, T) \right]$$

where p_e is the degeneracy of lowest electronic level and p_n the degeneracy due to nuclear spin.In the case of a polyatomic molecule with n independent rotating parts, Halford¹⁴ has proposed the following expression for the rotational entropy:

$$S_{\text{rot.}} = R \ln \frac{1}{\pi\sigma} \cdot \left[\frac{8\pi^2 (A_1^a A_2^b A_3^c \dots A_n^a)^{1/n} \cdot kT e^{-n/2}}{h^2} \right],$$

where A_1, A_2, A_3, \dots are the moments of molecule and its independent rotating parts, a, b, \dots are the rotational degrees of freedom associated with the corresponding moments of inertia; $a + b + c = n$ the total number of rotational degrees of freedom. The vibrational entropy is expressed by the equation

$$S_{\text{vib.}} = R \sum_{i=1}^{i=3N-3-n} \frac{h\nu/kT}{e^{h\nu/kT} - 1} - \ln (1 - e^{-h\nu/kT}).$$

¹² Mayer, Brunauer and Mayer, *J.A.C.S.*, 1933, **55**, 37.¹⁴ Halford, *J. Chem. Physics*, 1934, **2**, 694.

In calculating the equilibrium constants given in Table II. by means of these methods, the procedure has been to use, wherever possible, the vibration frequencies as taken from Raman Spectra data. The moments of inertia, if not available from spectral data, were estimated from the known structures of the molecules and the interatomic distances as given by Sidgwick.¹⁸ The moment of the methyl group was taken as 0.0517×10^{-38} C.G.S.

Comparison of (1) and (2) leads to

$$\ln \frac{A_1}{pZ} = f(T) + C$$

and by inserting the values of A , and Z , p can be evaluated if $f(T) + C$ is known.

The following tables give the values of p obtained by these methods.

The tables may be conveniently considered in three sections; *1a*, in which the equilibrium constants have been calculated directly from molecular properties; *1b*, the equilibrium constants have been experimentally determined; *1c*, reactions in which the steric factor has been calculated from the measured reaction rates. All reactions listed are for the gaseous state.

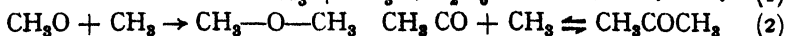
It can be readily seen from the tables that association reactions (which do not occur via an electron switch) involving simple molecules or atoms have values of the steric factor approaching unity, whereas those between complex molecules or radicals involving a large number of degrees of freedom have small steric factors. This is in close agreement with the theory given. It would be expected on this theory, that the steric factor would increase in the order of the complexity of the associating molecules. The experimental data (Table *1c*) provide strong support for this conclusion—the obvious discrepancies are most certainly due to the fact that the measured reaction is not simple and that the resulting polymer is a mixture of unknown composition. Furthermore, in all reactions between hydrocarbons or hydrocarbon radicals with the formation of a carbon-carbon bond, three degrees of translation and three degrees of rotation in the initial state are transformed into five vibrations in the transition and also the same type of restriction of position is necessary in the transition state. In any series of such reaction therefore, it is not to be expected that large decreases of the steric factor would be observed after the first few members, since the addition of another— CH_2 will produce only small increases in the moments of inertia of the reacting molecules.

It will be convenient here to summarise the conclusions reached :

1. The very much smaller steric factor of bimolecular association reactions of complex molecules compared with the reaction of simple molecules or atoms arises from the decreased probability of the transition state in these cases.

2. The steric factor will, in general, for a series of similar reactions, be more effective the greater the complexity of the reacting molecules.

In the general case of the reaction between complex molecules this second postulate will, however, not always be valid, since another factor—the restriction of position of the reacting molecules may be important. It may be stated that the narrower the restriction the smaller the steric factor. This can be illustrated by comparing the association reactions



¹⁸ Sidgwick, *The Covalent Link in Chemistry*, Cornell University Press.

Although the second reaction involves the more complex molecules it appears (Table II.) that it does not require a smaller steric factor. The reason for this is made apparent by a consideration of the nature of the transition state. At the top of the potential barrier the system will have three degrees of translational freedom, three of rotation and also one degree of motion along the co-ordinate of reaction. Motion along the latter co-ordinate corresponds to a decrease in potential energy, whereas a change in any other co-ordinate will involve an increase in potential energy. The remaining $3N - 7$ degrees of freedom will be vibrations or internal rotations and thus the system at the top of the barrier will be in a potential hollow of $3N - 7$ dimensions.

Now the probability of the associated state will be proportional to the number of states in which the molecule can exist, *i.e.*, to the volume of phase space corresponding to the transition state. The greater the restriction of position placed upon the molecules in the collided state the smaller will be this probability and thus the smaller the steric factor.

Returning to the examples (1) and (2) we can see qualitatively how the difference arises. In the first case two centres from each of which three valencies branch become linked together and this will impose a greater restriction of position in the transition state than in the second case where the two centres are linked by an atomic bridge ($-O-$). From this effect alone reaction (1) will require an increased steric factor. Hence, the third conclusion is (3) the greater the restriction of position of the molecules in the transition state the smaller the steric factor.

Steric Hindrance.

Up to the present the steric factor has been considered only in relation to changes in the probability of the collided state which are not caused by changes of energy. Sometimes, however, the steric factor may make its appearance as an energy term. This immediately leads us to the important question of steric hindrance, examples of which are well known. In these cases it is to be expected that the steric effect will appear in the energy term rather than a probability term independent of the energy.¹⁶

Finally, as an illustration we shall outline the application of our theoretical results to the cracking of hydrocarbons.*

Cracking of Hydrocarbons.

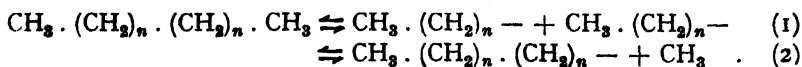
The decomposition of long chain saturated hydrocarbons occurs via the fracture of a carbon-carbon bond. Investigation with the simpler hydrocarbons shows that there is a certain probability that any one of the carbon-carbon bonds may break giving rise to a complex mixture of products. The thermal decomposition of the higher hydrocarbons have been little studied on account of the analytical difficulties, but in cases that have been investigated the results seem to indicate that the products resulting from the scission at the centre of the chain are more abundant.¹⁷

¹⁶ Hinshelwood and Legard (*Journ. Chem. Soc.*, 1935, p. 595) have recently obtained experimental evidence in certain esterification reactions that steric hindrance depends on high activation energy rather than on the factor p .

* A paper on the application to polymerisation reactions was read at the Faraday Society's Discussion on Polymerisation and Condensation, September, 1935, and will be published in this Journal.

¹⁷ Sachaner and Tilicheyer, *Chemistry and Technology of Cracking*, Chem. Catalog. Co., 1932.

From our previous consideration we see that the decomposition of a long chain hydrocarbon, the more complex the products the slower will be their velocity of association, *e.g.* if we compare the two reactions



then the rate of association of the products in reaction (1) will be slower than (2) and also since in the reverse reaction the same type of bond is broken in both cases, the equilibrium of (1) will be shifted further to the right than that of reaction (2). The final products of hydrocarbon decomposition will be determined by a set of reactions of the type (1) and (2), and if we make the assumption that equilibrium is established in these reactions, then it clearly follows that the products of reaction, in which the initial stage is the dissociation into complex radicals may be more abundant than those of reactions in which a simple radical is initially produced.

In conclusion, the author wishes to express his indebtedness to Professor M. Polanyi for many helpful suggestions.

Summary.

A consideration of the reaction velocity constant by means of the transition state method leads to a direct interpretation of the large steric factor of bimolecular association reactions. The steric factor is shown to be related to the probability of the transition state, and it is concluded that the small steric factor of bimolecular associations between complex molecules compared to those of atoms or simple molecules arises from the decreased probability of the transition state in these cases. The application of these views to the rupture of long chain molecules is indicated.

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THE CATALYTIC DECOMPOSITION OF HYDROGEN PEROXIDE ON DIFFERENT METALS.

By JOSEPH WEISS.

Received 23rd July, 1935.

The catalytic decomposition of hydrogen peroxide into water and molecular oxygen was first studied by Thenard and has since been investigated in great detail. Bredig and his collaborators¹ studied the reaction on solid and colloiddally dispersed metals. Though a great deal of interesting experimental material has been collected, the mechanism of this catalysis is still unexplained.

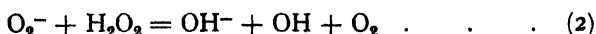
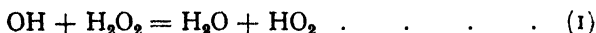
The velocity of the chemical reaction on the interface is often considerably greater than the rate of diffusion of the reacting molecules or the reaction products to or from the interface. In this case we are really measuring the rate of diffusion.² In other cases the velocity depends on

¹ Bredig and Müller von Bernek, *Z. physik. Chem.*, 1899, **31**, 258; Bredig and Ykeda, *Z. physik. Chem.*, 1901, **37**, 1; Bredig and Teletow, *Z. Elektrochem.*, 1906, **12**, 581.

² Nernst and Brunner, *Z. physik. Chem.*, 1904, **47**, 53; 1905, **51**, 95.

the adsorption of the hydrogen peroxide on the surface, and when the surface is practically saturated, the velocity becomes independent of the concentration of H_2O_2 . Owing to these reasons it is often practically impossible to draw any conclusions about the mechanism from the dependence of velocity on concentration as in homogeneous systems.

An opportunity to investigate the problem from a new point of view arose from the work of Haber and Weiss³ on the catalytic decomposition of H_2O_2 in homogeneous systems. Here the H_2O_2 is primarily attacked monovalently, yielding the radicals OH or HO_2 (O_2^-) which may further give rise to the chain reactions:



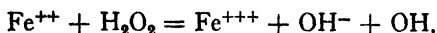
Recent experiments on the dependence of the catalytic decomposition on the H^+ ion concentration have shown that the original equation (2) must be altered so that the radical HO_2 is replaced by its anion O_2^- . They are related by the dissociation equilibrium:



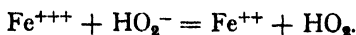
with the equilibrium constant

$$\Gamma_{\text{HO}_2} = \frac{[\text{O}_2^-][\text{H}^+]}{[\text{HO}_2]}$$

In homogeneous systems the primary formation of the radicals with the consequent initiation of the chains can be accomplished in many different ways; for instance, by the transformation of a metal ion into one of next higher valency, as in the case of ferrous ion:³



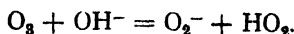
or by reduction of a higher valent state, as in the case of the ferric catalysis:³



Hydrogen peroxide can also be split by the action of a light quantum⁴



or the radicals HO_2 and O_2^- may be produced by the reaction between ozone and an OH^- ion⁵



General Theory.

The action of the atoms of the metal surface is considered to be similar to that of metal ions where the formation of the radicals is taking place as a result of a simple electron transfer process.

According to the Pauli-Sommerfeld theory every metal can be considered as a reservoir of quasi free electrons which obey the Fermi-Dirac statistics.

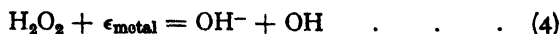
The most simple assumption is that the electrons of the metal electron

³ F. Haber and J. Weiss, *Proc. Roy. Soc.*, 1934, 147A, 332, also Haber and Weiss, *Naturwiss.*, 1932, 20, 948.

⁴ Urey, Dawsey and Rice, *J.A.C.S.*, 1929, 51, 1371; G. Kornfeld, *Z. physik. Chem.*, 1935, 29B, 205. Haber and Weiss, *loc. cit.*³

⁵ J. Weiss, *Trans. Faraday Soc.*, 1935, 31, 668.

gas are able under certain circumstances to split the H_2O_2 molecules present at the interface metal/solution according to :



Here the hydrogen peroxide is acting as an oxidising agent being itself reduced monovalently by an electron from the metal.

In alkaline solutions of H_2O_2 which contain a larger quantity of the anion HO_2^- , the process :



may become important where the anion gives an electron to the metal. Here the hydrogen peroxide is acting as a reducing agent in the form of its anion HO_2^- . This is related to the H_2O_2 by the dissociation equilibrium :



with the dissociation constant

$$K_{\text{H}_2\text{O}_2} = \frac{[\text{HO}_2^-][\text{H}^+]}{[\text{H}_2\text{O}_2]} \quad (20^\circ \text{C.})$$

Processes (4) and (5) clearly show the two different types of reactions which hydrogen peroxide can undergo ; namely reduction and oxidation.

We will here deal with reaction (4) in detail. The important point is that OH radicals are formed when H_2O_2 is attacked monovalently so that one electron is transferred. The following experiments indicate that the simultaneous formation of two OH^- ions according to the reaction



is obviously not taking place to a great extent. This fact can be easily explained on the basis of the Franck-Condon principle.

In the figure the potential curves are reproduced schematically for two OH radicals, one OH radical and one OH^- ion, and for two OH^- ions. One can understand that the formation of OH^- ion and OH radical from H_2O_2 molecule ($a \rightarrow b$) is, from energy reasons alone, very much favoured compared with the simultaneous formation of two OH^- ions ($a \rightarrow c$). This is due to the strong Coulombic repulsive energy between the two OH^- ions ; even if we assume a value of 2 Å. for the distance between the OH in the H_2O_2 molecule, this is of the order of ~ 7 volts.

A potential barrier at the metal surface prevents the electrons from escaping from the metal. Transfers of electrons are essentially possible only between levels of equal energy.

We will denote by ϕ the work function of the metal under the given conditions, i.e., the negative energy of the highest occupied level in the metal, by E_{OH} the electron affinity of the OH^- ion and by $D_{\text{H}_2\text{O}_2}$ the dissociation energy of H_2O_2 into two OH radicals. ΔA stands for the difference of the adsorption energies between the initial state (H_2O_2) and the final state ($\text{OH} + \text{OH}^-$) on the metal surface under consideration

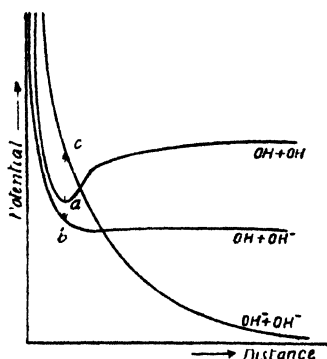


FIG. 1.—Schematic diagram of the potential curves.

(ΔA will practically always have a positive value because of the strong adsorption of the free radical OH). Then the energy necessary for the electron to split the H_2O_2 is given by $E = D_{\text{H}_2\text{O}_2} - E_{\text{OH}} - \Delta A$. This value of E must lie in the continuum of the occupied electronic levels within the metal, i.e., the relation :

$$E_{\text{OH}} + \Delta A - D_{\text{H}_2\text{O}_2} > \Phi \quad (7)$$

must be fulfilled.

Equation (7) can be tested experimentally since it is possible to alter both Φ and ΔA arbitrarily.

Catalytic Decomposition by Electrolysis.

The most simple and direct method to alter Φ is to apply a negative potential ($-V_e$) to the metal surface concerned. This negative potential will decrease the work function of the metal to the value of the order

$$\Phi' = \Phi - eV_e,$$

and will therefore favour the electron transfer.⁶

Mercury and bright platinum are not effective catalysts for the decomposition of H_2O_2 in acid solution. But if we favour, by cathodic polarisation, the escape of the electrons from the metal, we find an entirely new effect, which could hardly be expected on earlier views. We get a much stronger catalytic decomposition than on the unpolarised metals under the same conditions.

The experiments were made in an apparatus of the following description. It consisted essentially of a glass bell in a glass beaker, provided with a cooling spiral for the regulation of temperature, which could be read on the thermometer and kept constant to $\pm \frac{1}{2}^\circ \text{C}$. The cathode, Pt or Hg (amalgamated platinum), was built in the form of a rapid stirrer which was introduced through an air-tight joint.

The gas evolved was collected in a gas burette and hydrogen and oxygen determined in the usual way after a qualitative test to show the absence of other gases. The cathodic gases contain either pure hydrogen, mixtures of hydrogen and oxygen, or pure oxygen. The surprising result is the appearance of oxygen on the cathode. Some of the experimental results are collected in Table I.

We see that in the most favourable case about 4 mols O_2 per 1 Faraday can be obtained. These high values are however not always easily reproducible as the individual processes are very dependent on the state of the metal surface. But values of about 2 mols O_2 per 1 Faraday are always easily obtained (see Table I.).

We have here, probably for the first time, a very noticeable departure from Faraday's law caused by secondary processes. This corresponds to the well-known apparent break-down of the Einstein law in photochemistry.

In Table II. some results have been calculated from the older work of Tanatar.⁷ But Tanatar was working only with low values of the ratio $\frac{[\text{H}_2\text{O}_2]}{[\text{H}_2\text{SO}_4]} = \gamma$ (see experiments Tables I. and II.), so that he did not find the effect which we have observed. However, as he made no analysis of his cathode gas, the assumption that it was pure H_2 is open to doubt.

For the sake of completeness we should mention briefly the anode process in the electrolysis of hydrogen peroxide. As in the experiments of Tanatar,⁷ which we have confirmed in acid solutions, one always obtains a maximum value of 1 mol. O_2 per Faraday. Since the formation of OH

⁶ Cf., R. W. Gurney, *Proc. Roy. Soc.*, 1932, **137A**, 134.

⁷ S. Tanatar, *Ber.*, 1903, **36**, 199.

TABLE I.—ELECTROLYSIS OF HYDROGEN PEROXIDE IN SULPHURIC ACID SOLUTION (20° C.)

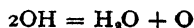
Nr.	[H ₂ O ₂] Mols./ltr.	[H ₂ SO ₄] Mols./ltr.	$\gamma = \frac{[H_2O_2]}{[H_2SO_4]}$	Current Amps./cm ² .	Volume Per Cent. O ₂ in Cathode Gas.	Mols. O ₂ * Per 1 Faraday.	Remarks.
1	0.445	0.119	3.74	0.053	34	7.54 · 10 ⁻³	platinum cathode
2	0.407	0.119	3.45	0.026	16	5.70 · 10 ⁻³	
3	0.482	0.012	41.6	0.013	88	2.03 · 10 ⁻¹	
4	0.360	0.0625	5.76	0.026	19	1.0 · 10 ⁻¹	
5	0.350	0.0625	5.65	0.040	10	5.0 · 10 ⁻³	
6	0.216	0.119	18.10	0.010	20	3.0 · 10 ⁻³	
7	0.233	0.0119	19.60	0.040	13	3.0 · 10 ⁻³	mercury cathode (amal- gam pla- tinum)
8	0.500	0.0115	43.5	0.010	60	6.0 · 10 ⁻³	
9	0.532	0.0115	46.3	0.030	82	2.7 · 10 ⁻¹	
10	0.800	0.0111	72.1	0.030	100	1.5 · 10 ⁻¹	
11	0.941	0.0005	1882	0.0040	100	3.93	
12	0.941	0.0005	1882	0.0045	100	2.23	
13	0.470	0.0005	940	0.0067	100	2.10	
14	0.470	0.005	94	0.024	100	0.44	
15	0.050	0.001	50	0.007	100	0.19	
16	0.021	0.005	4.2	0.023	practically no gas on the cathode		

* The values are corrected for the oxygen obtained in blank experiments without current. This correction can be practically disregarded for mercury cathodes.

TABLE II.—ELECTROLYSIS OF HYDROGEN PEROXIDE IN SULPHURIC ACID SOLUTION (20° C.).

Nr.	[H ₂ O ₂] Mols./ltr.	[H ₂ SO ₄] Mols./ltr.	$\gamma = \frac{[H_2O_2]}{[H_2SO_4]}$	Current in Amps.	Mols. H ₂ per 1 Faraday on the Cathode.	Mols. O ₂ per 1 Faraday on the Anode.	Remarks.
1	0.44	1.53	0.287	0.268	0.4	0.85	platinum elec- trodes
2	0.88	1.53	0.574	0.146	0.15	1.0	
3	1.76	1.53	1.148	0.201	0.003	1.02	

radicals on the anode can be assumed, the process may be represented by the reaction



which was found for the gaseous state by Bonhoeffer and Pearson.* This is followed by the decomposition of H₂O₂ by oxygen atoms :

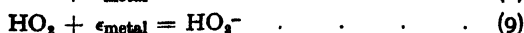


In alkaline solutions where HO₂⁻ ions can also be discharged on the anode we should still expect short chains. Some experiments in this direction seem to confirm this, but we will not discuss these further here.

The primary process on the platinum cathode (as also for the mercury in acid solution) is represented by equation (7). The OH radicals thus formed can initiate the chain reactions (1 and 2) which proceed on the surface of the metal causing the decomposition of H₂O₂ into molecular oxygen and water.

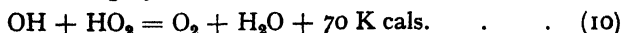
* Bonhoeffer and Pearson, *Z. physik. Chem.*, 1931, **14B**, 1; also Rodebush and Wahl, *J. Chem. Physics*, 1933, 1.

There are also some chain breaking processes which we have to take into account. The following processes:



as well as reaction (4) are favoured by a negative potential.

Owing to the comparatively high concentration of the radicals on the surface, chain breaking by the interaction of two radicals, *e.g.*,



may assume an important part. From all these considerations we have to expect only short chains on the surface, and is in agreement with experiment.

A mechanism for the catalytic decomposition of hydrogen peroxide has been assumed which involves chain reactions occurring in the adsorbed phase on the surface of the catalyst. Due to the high adsorption energy of free radicals, a diffusion of the chains from the surface into the solution (at the comparatively low temperatures used) is very improbable. This could only occur appreciably if the surface became saturated with radicals. There is, however, no experimental evidence for this effect. There seems to be no theoretical objection to the assumption of surface chains and the application of the method of stationary concentrations which has already been discussed in a previous paper by J. A. Christiansen.⁹

Reactions (4), (8) and (9) may also be regarded as an intermediate formation of positive ions on the metal surface according to:



The electrons used up are replaced by the electric current.

From the reactions (1), (2), (4), (8), and (9) one can derive an expression for the rate of evolution of oxygen in the stationary state on the cathode during electrolysis.

For the oxygen evolved per 1 Faraday (F) we obtain the differential equation:

$$\frac{d(\text{O}_2)}{dF} = \frac{k_2[\text{O}_2^-]}{2k_4 + k_2[\text{O}_2^-] \left\{ 1 - \frac{[\text{H}^+]}{K_{\text{HO}_2}} \right\}}.$$

If $2k_4 \gg k_2[\text{O}_2^-] + \left\{ 1 - \frac{[\text{H}^+]}{K_{\text{HO}_2}} \right\}$ which practically always is the case in acid solution, then:

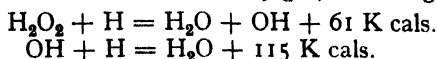
$$\frac{d(\text{O}_2)}{dF} \sim \text{prop} \frac{[\text{H}_2\text{O}_2]}{[\text{H}^+]} \sim \text{prop} \frac{1}{\gamma}.$$

One can see from Table I. that this relation is confirmed qualitatively by the experiments. The amount of oxygen liberated per 1 Faraday decreases with the ratio γ .

In more acid solutions (γ small) the reactions which we have considered above are not sufficient to describe completely the cathodic process. The experiments show that the discharge of hydrogen ions and the recombination of the hydrogen atoms to hydrogen molecules becomes important and thus with decreasing γ we obtain a mixture of O_2 and H_2 up to practically pure H_2 .

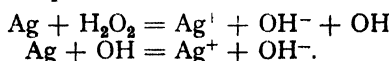
⁹ J. A. Christiansen, *Z. physik. Chem., Bodensteinfestband*, 1931, 69.

In these cases a smaller or greater part of the hydrogen peroxide is reduced to water without evolution of any gas, according to the equations :



Catalytic Decomposition on Silver.

The reaction on solid silver has been studied by McIntosh¹⁰; Wiegel¹¹ has investigated the catalytic decomposition in the presence of colloidal silver. We have here the same type of reactions. The colloidal metal partly dissolves in hydrogen peroxide without appreciable evolution of gas according to the equations :



Hydrogen peroxide is here acting as an oxidising agent. As the colloidal silver is increased and is finally present as a solid phase, the reaction



can take place to a considerable extent, so that silver and HO_2 radicals are produced. The latter start the chain reactions (2) and (1) and give rise to a strong catalytic decomposition of the H_2O_2 . The silver formed deposits on the colloidal particles present and by increasing their size changes the colour of the solution. Reaction (12) is independently confirmed by the well-known reducing action of H_2O_2 on silver salts in alkaline solutions.

For the stationary state :

$$\frac{d[\text{HO}_2]}{dt} = 0,$$

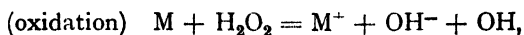
so that when silver is present as a solid phase we get from equation (12) the relation

$$[\text{Ag}^+][\text{HO}_2^-] \cong \text{const.}$$

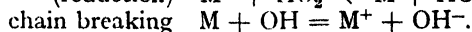
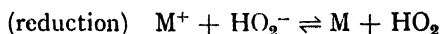
This relation was proved experimentally by Wiegel, but this author could not give a satisfactory explanation of his results.

Catalytic Decomposition on Platinum, Gold and Palladium.

The following five reactions, already represented by equations (1), (2), (4), (5) and (8), are sufficient to describe the catalytic decomposition on these noble metals in the solid and colloidal states ($M = \text{Pt, Au, Pd}$)



chain reactions (1) and (2)



We obtain according to the above equations for the rate of catalytic decomposition in the stationary state the relation :

$$-\frac{da}{dt} = 4k_4 \frac{[\text{H}^+]}{[\text{H}^+] - I_{\text{HO}_2}^r} [\text{H}_2\text{O}_2] \quad . \quad . \quad . \quad (13)$$

¹⁰ D. M. McIntosh, *J. Physic. Chem.*, 1902, **6**, 15.

¹¹ B. Wiegel, *Z. physik. Chem.*, 1929, **143A**, 81.

where a denotes the analytical concentration in mols./litre of hydrogen peroxide present in the solution. Its relation to the real concentration $[H_2O_2]$ is given by :

$$[H_2O_2] = \frac{a[H^+]}{K_{H_2O_2} + [H^+]}$$

Equation (13) can be tested by experiment in various ways.

One of the most striking features of the catalytic decomposition on these colloidal and solid noble metals is the fact that there is a maximum rate of decomposition for a certain optimum hydrogen ion concentration. This is in the range of about $p_H \sim 12$. In stronger acid or alkaline solutions the H_2O_2 is rather stable.

The hydrogen ion concentration was plotted against the time required for a 50 per cent. change in H_2O_2 concentration (for a given concentration of H_2O_2). In Table III. the values which can be obtained from these curves for the optimum H^+ concentration are summarised.

TABLE III.

Metal.	Optimum $[H^+]$ Conc. $[H^+]_{max.}$	Conc. $[H_2O_2]$ Mols./litr.	Author.
Platinum (colloidal) $3.3 \cdot 10^{-6}$ mols./litr.	5.0×10^{-13}	0.022	Bredig and Müller v. Berneck
Platinum (platinised sheets)	3.2×10^{-13}	0.125	Rius ¹²
Gold (colloidal) $1.25 \cdot 10^{-6}$ mols./litr.	6.0×10^{-13}	0.045	Bredig and Reinders ¹³
Palladium (colloidal) $1 \cdot 10^{-6}$ mols./litr.	1.6×10^{-13}	0.100	Bredig and Fortner ¹⁴

The existence of an optimum H^+ concentration can easily be deduced theoretically. Differentiating equation (13) with respect to the $[H^+]$ and putting the first differential quotient equal to zero we obtain :

$$[H^+]_{max.} = \frac{K_{H_2O_2} \Gamma'_{HO_2}}{K_{H_2O_2} - \Gamma'_{HO_2}} \quad (14)$$

Assuming that the dissociation constant of hydrogen peroxide has about the same value in the adsorbed phase as in the homogeneous phase ($K_{H_2O_2} = 1.2 \times 10^{-12}$ (20° C.) we can calculate the constant of electrolytic dissociation for the HO_2 radical in the adsorbed phase from the equation (14). We obtain :

$$\Gamma'_{HO_2} \sim 10^{-13} \text{ (20° C.)}$$

This differs appreciably from the dissociation constant in homogeneous aqueous solution which has been shown to be ¹⁵

$$\Gamma_{HO_2} \sim 10^{-6} \text{ (20° C.)}$$

¹² A. Rius, *Z. Electrochem.*, 1930, **36**, 149.

¹³ Bredig and Reinders, *Z. physik. Chem.*, 1901, **37**, 323.

¹⁴ Bredig and Fortner, *Ber.*, 1904, **37**, 798.

¹⁵ J. Weiss, *Trans. Faraday. Soc.*, 1935, **31**,

This difference can easily be explained as the free radical HO_2 is certainly more strongly adsorbed on the surface than the ions H_3O^+ and O_2^- so that the equilibrium (3) is displaced towards the undissociated product.¹⁶

According to equation (14) $[\text{H}^+]_{\text{max}}$ should (to a first approximation) be independent of the concentration of H_2O_2 and of the nature of the metal. These conclusions are in good agreement with experiment (see Table III.).

According to what has already been said we are able, by changing Φ or ΔA , to alter the rate of transfer of electrons (rect. 4) and thus to influence the velocity of decomposition.

The poisoning influence of substance such as KCN, Na_2S CO can also be easily explained. These substances probably form a sort of co-ordination surface compound, with the metal atoms on the surface. Then we know from magnetic researches on the halides and complex compounds of platinum and palladium that "inert gas" electron shells are often formed.¹⁷ The separation of an electron from these now completed electron shells of the metal atom on the surface requires a high energy of the order of magnitude of the ionisation potential of an inert gas. This practically prevents the occurrence of electron transfer processes so that the decomposition of H_2O_2 is no longer possible.

Catalytic Decomposition on Zinc.

When, in addition to its catalytic action, the metal is attacked to an analytically determinable amount, it is necessary to supplement these more physical considerations by chemical ones.

Since the investigations of Schönbein¹⁸ and M. Traube¹⁹ on the formation of hydrogen peroxide in the autoxidation of Zn, Cd, Fe, etc., in the presence of water, it has been a generally accepted fact that these base metals—in contradistinction to the noble metals—have no catalytic effect in the decomposition of H_2O_2 . This fact would be very difficult to understand from our theoretical point of view. But as shown by the following experiments, this conclusion is by no means generally true.

In investigating the reaction between metallic zinc and hydrogen peroxide in neutral and (sulphuric) acid solutions, we were able to detect, under suitable conditions, a decided catalytic decomposition of H_2O_2 . Hydrogen peroxide formed in the autoxidation of zinc and other metals has been found only in small concentrations. This is now to be understood as the stationary state resulting from the formation and decomposition reactions. Some characteristic cases, selected from a larger number of experiments, are given in Table IV.

The experiments were carried out as follows: a definite quantity of pure zinc (granules) was added to a neutral or acid solution of hydrogen peroxide in a suitable shaking apparatus equipped with a gas-outlet, and shaken in a thermostat. The gaseous reaction products were collected in a gas burette and hydrogen and oxygen were determined in the usual way. Hydrogen peroxide and the free acid were titrated. On varying the experimental conditions it is possible to obtain as the gaseous products either practically pure H_2 (small ratios γ), various mixtures of H_2 and O_2 , or no gas at all. In the solution we find as reaction products water,

¹⁶ Cf. Deutsch, *Z. physik. Chem.*, 1928, **136**, 353; H. Freundlich, *Kapillar-chemie*, II Aufl. (1931).

¹⁷ Stoner, *Magnetism and Matter* (Methuen & Co. Ltd., London, 1934).

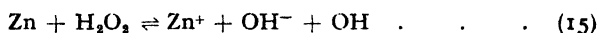
¹⁸ Schönbein, *J. prakt. Chem.*, **71**, 285; **78**, 63; **79**, 65.

¹⁹ M. Traube, *Ber. deutsch. Chem. Ges.*, 1893, **26**, 1474; 1885, **18**, 1894.

Zn^{++} — ions (ZnSO_4), and at low H^+ — concentrations a white precipitate, found to be essentially $\text{Zn}(\text{OH})_2$. According to the above considerations the surface reaction between zinc and H_2O_2 can be written in the form :

TABLE IV.—REACTION BETWEEN HYDROGEN PEROXIDE AND ZINC METAL.

Nr.	$[\text{H}_2\text{O}_2]$ Mols./ltr.	$[\text{H}_2\text{SO}_4]$ Mols./ltr.	$\gamma = \frac{[\text{H}_2\text{O}_2]}{[\text{H}_2\text{SO}_4]}$	$-\frac{\Delta(\text{H}_2\text{O}_2)}{\Delta t} \cdot 10^3$ Mols./ltr./min.	$\frac{\Delta(\text{H}_2\text{SO}_4)}{\Delta t} \cdot 10^3$ Mols./ltr./min.	$\left[\frac{\Delta(\text{H}_2\text{O}_2)}{\Delta t}\right] \frac{\text{Zn}(\text{OH})_2}{\text{Mols./ltr./min.}}$ $\cdot 10^3$	$\left[\frac{\Delta(\text{H}_2\text{O}_2)}{\Delta t}\right] \frac{\text{H}_2\text{O}}{\text{Mols./ltr./min.}}$ $\cdot 10^3$	$\left[\frac{\Delta(\text{H}_2\text{O}_2)}{\Delta t}\right] \frac{\text{O}_2}{\text{Mols./ltr./min.}}$ $\cdot 10^3$	$\frac{\Delta(\text{H}_2)}{\Delta t} \cdot 10^5$ Mols./ltr./min.	$\frac{\Delta(\text{O}_2)}{\Delta(\text{H}_2\text{O}_2)}$
1	0.808	—	—	4.75	—	3.68	—	0.9	—	0.18
2	0.802	0.102	157.2	9.51	3.40	4.96	3.40	1.15	—	0.12
3	0.500	0.037	27.0	19.7	11.75	4.12	11.75	3.83	—	0.19
4	0.0965	0.037	5.2	10.8	9.87	0.488	9.87	0.453	—	0.042
5	0.813	0.416	3.8	32.6	308	5.70	308	5.25	0.252	0.016
6	0.189	0.392	1.8	400	454	—	389	4.44	54.2	0.011
7	0.805	in water free ether solution no observable change after 144 hours.								
8	0.825	in water free amyl alcohol solution no observable change after 24 hours.								



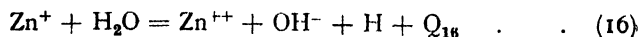
Assuming the monovalent course of the reaction, univalent zinc ions are formed.²⁰

Despite the relatively high ionisation potential of the second valency electron, it is well known that the monovalent Zn^+ ions cannot be detected in the solution. Obviously they disappear and so cause the strong observed attack of the Zinc (according to equilibrium 15).

One can think of many processes by which the primarily formed Zn^+ can undergo further reaction with the formation of Zn^{++} .

The reaction of Zn^+ with H_2O_2 or OH is sufficiently exothermal, and this is also true for the reaction $2\text{Zn}^+ = \text{Zn}^{++} + \text{Zn}$.

The results obtained with solutions of hydrogen peroxide in dry ether and amyl alcohol (see Table V., experiments 7 and 8) which gave no noticeable attacks even after 144 hours, show that great importance should be attributed to the decomposition with water (or perhaps with the H_3O^+ ions of the water) according to :



Q_{16} can be calculated from a cyclic process, and yields a value of $Q_{16} \sim 54\text{K cal.}$, so we see that reaction (16) is sufficiently exothermal.

Here again the ratio $\gamma = \left(\frac{[\text{H}_2\text{O}_2]}{[\text{H}_2\text{SO}_4]} \right)$ is important in deciding the course of the process, as can be seen from Table IV.

The circumstances here are very similar to those which have been discussed for the electrolysis of H_2O_2 and need not be considered in further detail.

Summary.

1. The initial process of the catalytic decomposition of hydrogen peroxide by metals involves an electron transfer from the metal to the H_2O_2 .

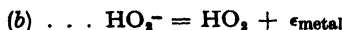
²⁰ Cf. A. MacAulay, *Nature*, 1930, 126, 914; S. V. Bodfors, *Z. physik. Chem.*, 1932, 160A, 115; 1931, 153A, 83.

adsorbed on the interface. The hydrogen peroxide is thereby attacked monovalently (*i.e.*, one electron is transferred), resulting in the formation of the radicals OH or HO₂. The chain reaction of the catalysis can then proceed. The catalytic decomposition can be described in this way by assuming only very simple elementary processes in the adsorbed phase.

2. The two principal reactions involved are :



where the H₂O₂ is acting as an oxidising agent.



where the H₂O₂ is acting as a reducing agent.

3. The following fact constitutes strong evidence in favour of this mechanism : the catalytic decomposition becomes considerably greater if the electronic work function of the metal is decreased (*i.e.*, reaction (a) is favoured) through cathodic polarisation.

4. The catalytic decomposition on platinum, gold, palladium, silver and zinc metal has been investigated in detail and discussed from the above-mentioned points of view.

In conclusion, I would like to thank Professor F. G. Donnan, F.R.S., very heartily for his continuous interest in this work, and Professor H. Freundlich for valuable discussions.

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THE CALCULATION OF DIPOLE INTERACTION.

By R. P. BELL.

Received 16th July, 1935.

The contribution of dipole interaction to the free energy of a dilute gas or solution can in principle be calculated by the standard methods of statistical mechanics. Such calculations have been carried out for gases by W. H. Keesom¹ and by H. Falkenhagen,² while approximate treatments for solutions have been given by P. Debye³ and by R. M. Fuoss.⁴

Both the methods and the results of such derivations are cumbersome, and a much simpler way of attacking the problem in the case of solutions has been proposed by A. R. Martin.⁵ Instead of considering in detail the mutual potential energy of pairs of dipole molecules, he focusses attention on one molecule. The remainder of the solution is then considered to be a continuous medium, and the effect of the remaining dipole molecules is represented by their effect on the dielectric constant of this medium. If D_0 is the dielectric constant of the pure solvent and D that of the solution, then the contribution of the dipole

¹ *Physik. Z.*, 1921, **22**, 129.

² *Ibid.*, 1922, **23**, 87.

³ *Handbuch Radiologie*, 1925, **6**, 638.

⁴ *J. Amer. Chem. Soc.*, 1934, **56**, 1027.

⁵ *Trans. Faraday Soc.*, 1934, **30**, 759.

energy to the difference of chemical potential is taken as the difference in the electrostatic energies of a single dipole molecule in media of dielectric constants D and D_0 .

This procedure is open to two obvious objections. Firstly the use of the macroscopic dielectric constant (measured at low field strengths) assumes the absence of saturation effects, and secondly the assumption of a uniform medium supposes a random distribution round the central dipole. Both these assumptions are only strictly valid if the orientation energy of two dipoles is always small compared with the thermal energy, which is not the case for most systems of practical interest. However, the first of these factors will tend to make the calculated energy too great, and the second to make it too small, so that it is possible that this method of calculation may give correct results under suitable conditions.

This is most easily investigated by applying both methods to a simple case, *e.g.*, a dilute gas of rigid non-polarisable spherical molecules, the dipole being situated at the centre of the molecule and the separation of its charges being small compared with the diameter of the molecule. This system has been treated strictly by Keesom.¹ If the equation of state of the gas is written in the form

$$pv = NkT \left\{ 1 + \frac{B}{v} + o\left(\frac{1}{v^2}\right) \right\} \quad (1)$$

the coefficient B is shown by Keesom to have the value

$$B = N \cdot \frac{2}{3} \pi d^3 (1 - 3.33 \times 10^{-1} x^2 - 1.33 \times 10^{-2} x^4 - 5.24 \times 10^{-4} x^6 - 1.58 \times 10^{-5} x^8 - 4.11 \times 10^{-6} x^{10} - \dots) \quad (2)$$

where

$$x = \frac{\mu^2}{d^3 kT},$$

N = number of molecules,

d = diameter of molecule,

μ = dipole moment.

The electrostatic energy of a spherical dipole molecule has been calculated by a number of authors⁶ but the only treatment entirely free from errors is that given by Kirkwood.⁷ For the particular case in which the charge separation of the dipole is small compared with the diameter of the molecule, Kirkwood's equation becomes

$$\Delta w = \frac{\mu^2}{d^3} \left\{ \frac{D_i - D}{2D + D_i} - \frac{D_i - 1}{D_i + 2} \right\} \quad (3)$$

where Δw is the change of electrostatic energy on transferring the dipole molecules from a vacuum to a medium of dielectric constant D , the dielectric constant inside a sphere of radius d having the constant

⁶ See *e.g.*, Martin, *Phil Mag.*, 1929, 8, 547. Bell, *J. Chem. Soc.*, 1931, 139. 1371; *Trans. Faraday Soc.*, 1931, 27, 797.

⁷ *J. Chem. Physics*, 1934, 2, 351. Both the earlier calculations were carried out by evaluating $\int DE^2 dv / 8\pi$ where E is the field in a volume element dv . Martin's derivation arbitrarily confines the integration to the space outside a spherical surface and employs an incorrect expression for the potential. The author's derivation extends the integration over the whole of space and uses the correct expression for the potential, but as pointed out by Kirkwood, the energy in the interior of the molecule was incorrectly evaluated and the final result is in error by a factor of 1/3.

value D_i . The model treated by Keesom corresponds to $D_i = 1$, and since for a dilute gas $D - 1 \ll 1$, equation (3) becomes

$$\Delta w = \frac{\mu^2}{d^3} \cdot \frac{1 - D}{3} \quad . \quad . \quad . \quad (4)$$

In the present case the polarisation of the gas is due to the presence of dipoles, and the value of d is thus clearly the distance of closest approach of two dipoles, *i.e.*, the diameter of the dipole molecule. The dielectric constant of a dilute gas at low field strengths is given correctly by Debye's theory, *i.e.*, if there are N dipoles in v c.c.,

$$\frac{D - 1}{3} = \frac{4\pi}{3} \cdot \frac{N}{v} \cdot \frac{\mu^2}{3kT} \quad . \quad . \quad . \quad (5)$$

and hence from (4)

$$\begin{aligned} \Delta w &= - \frac{4\pi N \mu^4}{9v k T d^3} \quad . \quad . \quad . \quad (6) \\ &= - \frac{4}{9} \pi d^3 k T \cdot \frac{N}{v} \cdot x^2 \end{aligned}$$

where

$$x = \frac{\mu^2}{d^3 k T}.$$

To obtain the dipole contribution to the free energy of the gas we must consider the annihilation of the dipoles one at a time,* giving

$$F_e = - \frac{4}{9} k T \pi d^3 x^2 \int_0^N \frac{N}{v} dN = - \frac{2}{9} k T \frac{N^2}{v} \cdot \pi d^3 x^2 \quad . \quad . \quad (7)$$

After the annihilation of the dipoles the system consists of a dilute gas of rigid spheres. The second virial coefficient of the original system is therefore given by⁸

$$\begin{aligned} B &= N \cdot \frac{2}{3} \pi d^3 + \frac{F_e v}{N k T} \quad . \quad . \quad . \quad (8) \\ &= N \cdot \frac{2}{3} \pi d^3 \{1 - \frac{1}{3} x^2\}. \end{aligned}$$

This agrees with Keesom's exact expression (equation (2)) provided that $x^2 \ll 1$: moreover, owing to the rapid convergence of the series in (2), equation (8) gives a reasonably accurate value for B provided that $x \leq 1$, which is much less stringent than the condition $x \ll 1$ which might have been anticipated. Nevertheless, if we are dealing with a gas at ordinary temperatures having a molecular diameter of 3 Å., equation (8) will only be a good approximation if $\mu < 1.05 \times 10^{-18}$, so that the application to gases is strictly limited. In all actual cases to which (8) is applicable the dispersion forces will be much more important than the dipole forces.⁹

Statistical treatments of the type employed by Keesom are at present only able to predict the equation of state correct to terms in $1/v$, since they only take into account binary interactions. There appears to be no reason why the validity of Martin's method should depend on the concentration, and provided the above condition is fulfilled it should be applicable to the calculation of dipole interaction even in concentrated

* It is not legitimate merely to multiply the value of Δw by the number of molecules, as was done in a previous note (Bell, *Trans. Faraday Soc.*, 1934, 30, 773).

⁸ See R. H. Fowler, *Statistical Mechanics*, Chapter IX.

⁹ See F. London, *Z. Physik*, 1930, 63, 245; *Z. physik. Chem.*, 1930, 11B, 222.

systems where the usual statistical methods are not available. The measured dielectric constant of the system will of course include the polarisability terms, and its use will thus provide an approximate method of allowing for the effect of the polarisability on the interaction, at least in cases where the interdipole forces are the predominant factor.

In the case of liquid mixtures Martin's treatment (using Kirkwood's value for the energy) leads to the equation

$$-kT \log \frac{a_1}{N_1} = \frac{\mu^2}{d^3} \left\{ \frac{D-1}{2D+1} - \frac{D_0-1}{2D_0+1} \right\} \quad (9)$$

where a_1 is the activity of the dipole substance in a mixture of mole fraction N_1 and dielectric constant D , and D_0 is the dielectric constant of the standard state, *i.e.*, either of the infinitely dilute solution or of the pure substance. (This assumes that the activity would be proportional to the mole fraction in the absence of the dipole forces.) In this case it is not possible to make any comparison with an exact treatment, but we may expect by analogy that the limits of validity of equation (9) are roughly defined by $\mu^2/d^3 D kT \leq 1$, the factor $1/D$ being a crude way of allowing for the effect of the medium on the inter-dipole forces. Thus if we are dealing with a dilute solution in benzene of molecules of 3 Å. diameter, equation (9) will only apply if $\mu < 1.48 \times 10^{-18}$, while if $d = 2$ Å., the condition is $\mu < 0.80 \times 10^{-18}$. On the other hand in solutions containing higher concentrations of dipole molecules the dielectric constant is higher, and equation (9) can be used more generally for calculating the variation of the dipole energy with the concentration. It is just in such concentrated solutions that the ordinary statistical methods fail.

Owing to the form of equation (2) we should expect equation (9) to fail rather suddenly as the dielectric constant passes below a certain critical value. This may account for one feature of Martin's results¹⁰ for the vapour pressures and dielectric constants of mixtures of dipole substances with benzene. When $\log \frac{a_1}{N_1}$ is plotted against $\frac{D-1}{2D+1}$ the points for high dielectric constants form good straight lines, while deviations suddenly appear as the composition of the solution approaches pure benzene.

Summary.

By comparison with a statistical treatment, the method proposed by Martin for calculating dipole interaction is shown to be valid for sufficiently small values of the dipole moment. It should be particularly valuable in concentrated systems where statistical treatment is difficult.

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¹⁰ A. R. Martin, *J. Chem. Soc.*, 1932, 2658; 1933, 1413; *Trans. Faraday Soc.*, 1934, 30, 759.

THE CONDUCTIVITIES OF SOME ACIDS AND OTHER SOLUTES IN PYRIDINE.

BY MANSEL M. DAVIES.

Communicated by C. R. BURY.

The original purpose of this work was to detect the influence of chemical factors in determining electrolytic conductivities by establishing cases in which these conductivities arise from solvate formation. Measurements were made in nitrobenzene, pyridine, and their mixtures, but largely owing to the irreproducibility of the conductivities in the examples studied (triphenylmethyl chloride, picryl chloride, benzoyl chloride, etc.) the results were unsuitable for quantitative treatment. Attention was therefore confined to solutions of acids in pure pyridine. The conductivities of picric, perchloric, nitric and hydriodic acids have been measured in pyridine: these results are reported in Part I, and some of the previous work mentioned, in Part 2.

Experimental.

A Hartley and Barrett cell ¹ having grey platinised electrodes, a standard resistance box (calibrated at the N.P.L.), and the ratio and resistance arms of a P.O. box connected through a 4-ohm metre bridge formed the four arms of the Wheatstone network. A simple one-valve oscillator provided ample current of practically pure sine-wave form for the bridge. The latter was earthed through a modified Wagner bridge; ² it is worth mentioning that practically the same condition could have been attained for a bridge with equal ratio arms by merely earthing the centre tapping of the output coil of the oscillator. Adjustment of mica and air condensers allowed the balance point to be read directly to 1 in 10,000. The agreement between the resistances obtained with different frequencies and with different ratios in the bridge (criteria employed for each resistance measured) showed that this determination was reliable to at least 1 in 1000.

The working temperature was 25° C.; although temperature constancy during a series was better than $\pm 0.01^\circ$, there is a somewhat greater uncertainty in the mean temperature maintained.

The cell constant was determined by measurement of aqueous KCl solutions over the dilution range 5000-500 litres per equivalent, adopting the procedure described by C. W. Davies and Grindley.³ The conductance equation given by Shedlovsky⁴ was employed after correction to the new figure for the absolute conductance of 1/10 "demal" KCl due to Jones and Bradshaw.⁵ Condensation in the cap of the cell was prevented by immersion in the thermostat. Wide rings of paraffin wax sealed around the glass tubes carrying the leads to the plates avoided any short-circuiting by a film of moisture.

Pyridine was prepared by repeated fractionation of "Analar" supply in an all-Pyrex apparatus, designed on the principle of the Bourdillon still. Caustic potash powdered from pure sticks, magnesium perchlorate, and alumina and silica gels were used at different times as drying agents:

¹ *J. Chem. Soc.*, 1913, **103**, 786.

² *J. Amer. Chem. Soc.*, 1928, **50**, 1054.

³ *Trans. Faraday Soc.*, 1929, **25**, 133

⁴ *J. Amer. Chem. Soc.*, 1932, **54**, 1424.

⁵ *Ibid.*, 1933, **55**, 1780.

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potash and alumina gel,⁶ used successively, were generally preferred. The solvent finally obtained usually distilled over a range of 0.02° C. and was of specific conductivity $6, \pm 2 \times 10^{-8}$.

The influence of water on the conductance of the solvent was examined by using it as a solute in a typical run.

Water Added Gra. per 1000 Gra. Pyridine.	Dilution Litres/gr. Mole.	Specific Con- ductance.
0.000	—	6.87×10^{-8}
0.072	248	8.46 "
0.139	128.3	10.12 "
0.229	78.1	14.62 "

It seems improbable that the solvent conductivity, $\kappa = 6.0 \times 10^{-8}$, can be due to anything other than residual water which, accordingly, must be present to about 2 parts in 10,000, *i.e.*, a concentration of approximately $M/100$. Passage of carbon dioxide through the cell had scarcely any effect on the conductivity of the

moist pyridine.

Von Hevesy⁷ removed the residual water after chemical drying by subjecting the solvent to electrolysis. This procedure was adopted on several occasions using an auxiliary cell, with platinum electrodes, kept in a desiccator. After maintaining a p.d. of 220 volts for 40-60 hours the solvent was directly fractionated into the conductivity cell from a little potash. The electrolysis involved slight oxidation and reduction of the pyridine, but those products not removed by the distillation are certainly non-conducting, as shown by the lowest conductance thus attained, $\kappa = 1.49 \times 10^{-8}$.

Part 1.

For the strong acids, with the exception of picric acid, the pyridonium salts were prepared as solutes.

Pyridonium perchlorate was separated according to Arndt and Nachtray⁸ but using only 4 *N* HCl and NaClO₄ to avoid traces of chloride. Recrystallised twice from 95 per cent. alcohol, the product contained no detectable chloride and after drying in an air oven at 110°, melted sharply at 297° (corr.). Three titrations using baryta and phenol phthalein gave equivalent weights 178.4, 179.5, 179.1. (Calc. for C₅H₅N · HClO₄, 179.5.)

The sample for the second series was obtained by two further recrystallisations and filtration through sintered glass. After drying, there was no change in melting-point. The two series of conductivities agreed within 3 in 1000.

Pyridonium nitrate was prepared by slowly adding 70 per cent. A.R. nitric acid to slight excess of pure pyridine and cooling well. Twice crystallised from alcohol, it was dried by a stream of dry air on a sintered glass filter and by standing in a vacuum desiccator. Equivalent wts. found: 141.5, 142.0. Calc. for C₅H₅N · HNO₃, 142.05. A fresh sample was prepared for the second series, eq. wt. 141.9. The melting-point of all samples was unsatisfactory (116.5-118°). The maximum deviation which can be detected from a free hand $\lambda \cdot \sqrt{c}$ curve for the two series is 1 per cent.

Pyridonium iodide was similarly prepared from freshly distilled constant-boiling acid. It was recrystallised from alcohol and washed with dry ether, before drying as for the nitrate. Equivalent wts. found, 206.8, 206.3. Calc. for C₅H₅N · HI, 207.0. It decomposed (about 180°) before melting. The two lowest points in both series deviate widely (up to 3 per cent.) from the curve through those at higher concentrations. This is almost certainly due to slight amounts of oxidation, detectable by the faint brown tinge assumed by the concentrated solution in the weight-pipette.

⁶ *J. Amer. Chem. Soc.*, 1913, **39**, 1603.

⁷ *Z. Electrochem.*, 1910, **16**, 672.

⁸ *Ber.*, 1926, **59**, 448.

Six independent series of measurements were made with picric acid, which was obtained as follows: (1) A good laboratory sample was thrice recrystallised from water, and the product dried in an air-oven at 80-90° and kept in a vacuum P_2O_5 desiccator. (2) First recrystallised from CCl_4 - $CHCl_3$ mixture. (3) Same as second. (4) Fresh B.D.H. sample recrystallised twice from CCl_4 . (5) Fourth again crystallised from CCl_4 . (6) Fourth crystallised from water. The purity of these samples as judged from melting-point and titration (phenol red) was satisfactory, but the divergence between any two of the series is far beyond the error in measurement—at 2,000 litres the points lie over a range of 4 per cent. The conductance of any particular solution remained constant over long periods of time and showed no change either on addition of relatively large amounts of water or after heating the solution to 60° for half-an-hour. At the same time, the λ -values are all some 80 per cent. higher than those reported by Walden, Audrieth, and Birr.⁹

Anomalies in the conductivities of picric acid solutions have been ascribed to varying adsorption on the electrodes.¹⁰ This factor may explain the unexpected decrease in slope of the $\lambda \cdot \sqrt{c}$ curves for this acid at high dilutions ($V > 10,000$ litres per gram mole.), whilst the smaller

TABLE I.

$c \times 10^5$.	λ .	$c \times 10^5$.	λ .	$c \times 10^5$.	λ .
Pyridonium Perchlorate.		Pyridonium Nitrate.		Pyridonium Iodide.	
1st Series ($\kappa = 3.01 \times 10^{-8}$)		1st Series ($\kappa = 5.48 \times 10^{-8}$)		1st Series ($\kappa = 13.8 \times 10^{-8}$)	
3.870	88.7 ₁	5.465	60.7 ₉	4.978	71.5 ₇
7.704	84.1 ₀	10.601	50.7 ₈	10.316	71.1 ₆
13.032	79.9 ₇	17.343	43.7 ₈	16.261	69.4 ₁
23.150	75.3 ₆	27.023	37.3 ₀	25.337	66.2 ₇
38.050	70.4 ₃	48.110	30.6 ₉	46.956	60.0 ₀
65.85	64.3 ₆	76.16	25.9 ₃	67.96	55.4 ₈
93.77	60.2 ₆	105.08	23.0 ₂	91.31	51.7 ₈
129.64	56.5 ₄	130.94	21.1 ₆		
2nd Series ($\kappa = 3.89 \times 10^{-8}$)		2nd Series ($\kappa = 7.20 \times 10^{-8}$)		2nd Series ($\kappa = 12.3 \times 10^{-8}$)	
3.604	89.3 ₈	3.323	68.6 ₈	4.681	73.0 ₀
7.182	85.2 ₀	6.445	58.6 ₁	9.762	72.8 ₀
12.924	80.6 ₆	11.806	48.5 ₇	15.772	70.2 ₄
22.702	75.7 ₃	20.383	41.5 ₂	24.041	66.8 ₇
39.766	70.4 ₆	37.240	33.6 ₈	43.023	60.9 ₁
65.90	64.4 ₇	59.70	28.3 ₉	61.53	56.8 ₄
115.63	57.9 ₇	81.48	25.2 ₆	89.95	52.4 ₂
		106.98	22.8 ₂		
$\Delta = 1.03$ per cent. per degree.		$\Delta = 0.37$ per cent. per degree.		$\Delta = 0.89$ per cent per degree	
<hr/>					
$c \times 10^5$.	λ .				
Pyridonium Picrate.					
14.76	64.2				
21.03	61.8				
25.28	60.2				
35.72	57.2				
48.40	54.2				
67.62	50.4				

⁹ *Z. physik. Chem.*, 1932, **160A**, 346.¹⁰ *Ibid.*, 1924, **112**, 407.

adsorption on grey platinum could account for the divergence from the results of the German workers. A series of mean values is quoted below from which measurements differ by less than 3 per cent.

Pyridonium sulphate, iodate, and ferrocyanide proved to be too sparingly soluble to allow of measurements in these cases. It was found that benzoic acid has a conductivity too small to provide an extension by this method of the Wynne-Jones treatment of dissociation constants¹¹ to this medium of d.c. 12.0.

TABLE II.

$c \times 10^6$	λ	γ	f	K
Pyridonium Perchlorate. $\lambda_0 = 94.5$.				
3.870	88.7 ₁	0.971	0.888	9.93×10^{-4}
12.92	80.6 ₆	0.907	0.812	7.54 ₀ "
22.70	75.7 ₃	0.868	0.763	7.52 ₄ "
38.05	70.4 ₃	0.825	0.714	7.54 ₀ "
65.85	64.3 ₆	0.776	0.653	7.50 ₁ "
93.77	60.2 ₆	0.744	0.609	7.53 ₄ "
115.6 ₃	57.9 ₇	0.728	0.582	7.60 ₇ "
<i>Best value</i> = <u>7.55₄</u> $\times 10^{-4}$				

Pyridonium Nitrate. $\lambda_0 = 98.6$.

3.323	68.6 ₆	0.715	0.910	$4.93_7 \times 10^{-3}$
6.445	58.6 ₁	0.615	0.885	4.90 ₈ "
10.60	50.7 ₈	0.537	0.864	4.92 ₃ "
17.34	43.7 ₂	0.466	0.841	4.98 ₃ "
37.24	33.6 ₈	0.364	0.800	4.97 ₂ "
59.70	28.3 ₉	0.311	0.771	4.90 ₁ "
105.08	23.0 ₂	0.256	0.732	4.95 ₅ "
<i>Mean value</i> = <u>4.95₇</u> $\times 10^{-3}$				

Pyridonium Iodide. $\lambda_0 = 86.7$.

15.77	70.2 ₄	0.867	0.799	5.64×10^{-4}
24.04	66.8 ₇	0.838	0.763	6.06 "
25.34	66.2 ₇	0.832	0.758	6.00 "
46.96	60.0 ₀	0.775	0.697	6.07 "
61.53	56.8 ₆	0.745	0.667	5.97 "
67.96	55.4 ₈	0.730	0.652	5.82 "
91.31	51.7 ₆	0.694	0.624	5.61 "
<i>Best value</i> = <u>5.9</u> $\times 10^{-4}$				

of at least two determinations for the most concentrated solutions over a range of some 10° .

$$\Delta = \frac{\kappa(25.00) - \kappa(t)}{\frac{1}{2}(\kappa(25.00) + \kappa(t)(25.00 - t))} \times \frac{100}{1}.$$

The value to be expected from the change of viscosity of pyridine over this range is 1.38 per cent. per degree.

Dissociation constants for the perchlorate, nitrate and iodide have been deduced by the method of successive approximations described by Fuoss and Kraus.¹² Taking the dielectric constant,¹⁴ $D = 12.01$, the viscosity¹⁵ $\eta = 0.00800$, the following constants for the Debye-Hückel

Some results for nitric and hydriodic acids at much greater concentrations in pyridine have been reported by Hantzsch and Caldwell.¹²

Results.

All solutions were made up by weight and the weights corrected to vacuum standard. Concentrations are expressed in gram equivalents per 1000 cm.³ of solution, whose density was always assumed equal to that of pyridine ($d_4^{25} = 0.9780$). On the assumption that the conductivity of the pyridine was due to residual water behaving as a weak acid, no solvent correction has been applied for these solutes. The value of κ , the specific conductivity of the solvent in reciprocal ohms, is given with each series. The temperature coefficients Δ are the mean

¹¹ *Proc. Roy. Soc.*, 1933, **140A**, 440.

¹² *J. Amer. Chem. Soc.*, 1933, **55**, 476 and Fuoss, *ibid.*, 1935, 488.

¹⁴ *J. Chem. Soc.*, 1935, 776.

¹⁵ *Z. physik. Chem.*, 1908, **61**, 228.

¹⁶ *I.C.T.*, **5**, 20.

activity expression, and the Onsager conductivity equation, are obtained :

$$\beta = 8.480, \delta = 1.54 - 1.75; \alpha = 3.822 \lambda_0 + 154.0.$$

The results of these calculations, using data taken directly from the previous tables are given in Table II. (γ = degree of dissociation. K = dissociation constant.)

These values of K should be compared with those for acetic acid in water,¹⁶ $K_{25^\circ} = 1.754 \times 10^{-5}$, and iodic acid in water,¹⁸ $K = 0.1686$.

¹⁶ *J. Amer. Chem. Soc.*, 1933, **55**, 655.

Part 2.

B.D.H. or Kahlbaum preparations of the solutes reported below were usually available and were used after at least two recrystallisations. The nitrobenzene was prepared both by repeated fractional distillation of the laboratory supply and by nitration below 20° of benzene purified for freezing-point determinations. The dry solvent was stood over silver oxide¹⁷ and finally distilled under 10 mm. pressure from alumina gel in an all-glass apparatus. When distilled slowly with avoidance of any ebullition, solvent of conductivity 1.70×10^{-8} was obtained. Pyridine was added to the nitrobenzene solutions from a weight-pipette in the form of a dilute solution in the latter solvent. The normal solvent correction has been applied in these cases.

Triphenylmethyl chloride was prepared by passing dry HCl gas into a benzene solution of purified carbinol. The solution was kept boiling in a distillation flask and the water produced removed in the vapour with the solvent distilling. After at least an hour of this treatment, the solution was transferred to a desiccator and finally evaporated by evacuation. The following figures were obtained for this solute in nitrobenzene :

$c \times 10^5$	7.52	61.04	95.80	168.3	334.5
	3.43	0.69	0.49	0.32	0.19

These are the final values reached after several hours slow increase (e.g., a total increase of 10 per cent. in 30 hours) in the conductivity of each solution.

Addition of pyridine gave results as follows :

$\frac{\text{Mols. pyridine added}}{\text{Mols. solute}}$	0.0	0.141	0.336	0.755	1.28	2.40
λ	0.187	0.222	0.239	0.275	0.342	0.405

The complex formation occurring in these solutions was also indicated by the negative temperature coefficient of the conductivities.

Picryl chloride had a negligible conductivity in nitrobenzene but showed a relatively greater increase with addition of pyridine; for $c = 1.695 \times 10^{-3}$,

$\frac{\text{Mols. pyridine added}}{\text{Mols. solute}}$	0.0	0.356	0.898	1.77	3.01	5.31	8.40
λ	0.012	0.043	0.093	0.174	0.260	0.339	0.430

From the normal temperature change of the conductivity, $\Delta = 2.0$ per cent. per degree, it would appear that complex formation is far more complete in this instance than for triphenylmethyl chloride. Repeated attempts were made to measure the conductivities of picryl chloride in pure pyridine. On contact, these substances produce a very dark red solution and an almost black solid, further solution of which occurs very slowly. Owing to the difficulty of ensuring complete solution of the solute, added in this case directly to the solvent in the cell from a container weighed on

¹⁷ *Z. physik. Chem.*, 1913, **84**, 513.

the microbalance, and the subsequent slow change of conductivity the results were very divergent. The results of series 3, 4 and 5, are shown in the accompanying plot of λ against \sqrt{c} (Fig. 1).

Benzoyl chloride proved to be an electrolyte of intermediate strength in pyridine. Four independent series were done with this solute which was fractionated immediately before use in an all-glass apparatus; two of these series agreed to ± 1 per cent. (curve A, Fig. 1) whilst the other two were consistently higher by 5-10 per cent. The results of the former series were treated by the method of Fuoss and Kraus¹⁸ and gave $\lambda_0 = 32.0 \pm 0.5$, $K = 1.30 \pm 0.02 \times 10^{-5}$. These results for benzoyl chloride are of particular interest in view of the well-known use of pyridine as a medium for acylation.

The irreproducibility of the conductivities in the above cases is possibly the result of the presence in the solvent of traces of water to which benzoyl

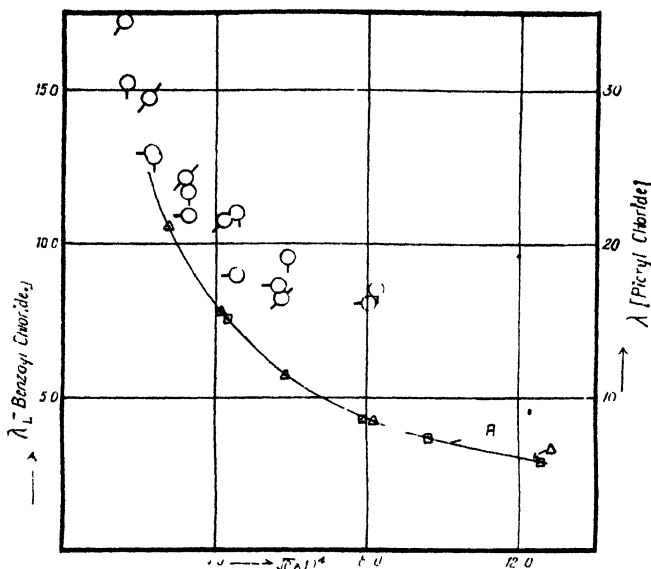


FIG. 1.—Curve A, benzoyl chloride Δ 2nd series, \square , 3rd series
 \odot , \odot , 3rd, 4th, and 5th series for picryl chloride.

pyridonium chloride would be particularly sensitive,¹⁹ whilst picryl chloride under certain circumstances is capable of opening the heterocyclic ring in pyridine.¹⁹

Most of the aromatic nitrocompounds form well-defined molecular compounds with nitrogen bases; this prompted the determination of some of their conductivities. *Meta*-dinitrobenzene had only a slight conductivity in pyridine (λ at 3500 litres = 0.45). The case of trinitrobenzene was of particular interest: it dissolved instantly in pyridine to a colourless solution which gradually developed a cherry-red colour, and the progressive increase of conductivity with time was undoubtedly correlated with this change. Series of measurements were made to follow the rate of complex formation from the conductivity change, and using Guggenheim's method of calculation,²⁰ a reasonably good unimolecular constant, $k = 6.3 \pm 0.3 \times 10^{-4}$

¹⁸ *Ber.*, 1919, **52**, 1463.

¹⁹ Hewitt, *Dyestuffs derived from Pyridine, etc* (Longmans, 1922), p 19, *et seq.*

²⁰ *Phil. Mag.*, 1926, **7**, 538

per minute, was obtained for the initial stages of the reaction. The following is a series of final values directly observed after the solutions had been in the cell at least 48 hours ($\kappa(\text{solvent}) = 9.2 \times 10^{-8}$):

$c \times 10^4$	1.384	2.758	5.480	10.84	21.47
λ	4.5	3.7	2.4	1.6 ₆	1.1 ₁

The partial suppression of the colour of these solutions on passage of HCl into the pyridine suggests that the ionisation is that of a weak acid. This is supported by the fact that trinitromesitylene dissolves in pyridine to a colourless solution, having no conductivity (at 1000 litres, $\lambda < 0.04$); it forms no addition compounds with pyridine bases (Beilstein).

The following were the "conductivities" measured for benzoic acid in pyridine ($\kappa(\text{solvent}) = 8.7 \times 10^{-8}$):

$c \times 10^4$	0.953	5.935	9.128	15.36	35.82
$\kappa(\text{solution})$	9.43	11.0	11.55	12.42	14.18
λ	0.070	0.038	0.030	0.024	0.015

A mean value for the dissociation constant of 1.6×10^{-10} can be calculated, but the conductivities relative to that of the solvent are obviously too small for this to have anything but qualitative significance.

Summary.

From conductivity measurements, the following dissociation constants for perchloric, nitric and hydriodic acids in pyridine have been determined, 7.55×10^{-4} , 4.96×10^{-5} and 5.9×10^{-4} , respectively, thus giving a quantitative measure of their relative strengths, and showing that nitric acid is appreciably weaker than the other two in this solvent. Certain "anomalous" electrolytes have also been investigated in pyridine.

I wish to record my indebtedness to Mr. C. R. Bury, M.A., B.Sc., for many valued criticisms and suggestions. I also wish to thank the Chemical Society for a grant, and the University of Wales for the award of a Research Studentship.

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THE ALLOTROPY OF PHOSPHORUS PENTOXIDE

BY A. N. CAMPBELL and A. J. R. CAMPBELL.

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Little is known definitely as to the Allotropy, or the polymorphism of phosphorus pentoxide. Mellor¹, and Newton Friend² give bibliographies, which reveal the conflicting nature of the data. Smits and Rutgers³ show that the ordinary amorphous powder is a mixture. We hold no brief either for or against Smits' theory of allotropy,⁴ but our work certainly shows that most forms of phosphorus pentoxide are

¹ Mellor, *Comprehensive Treatise on Inorganic Chemistry*, Vol. VIII., 940 *et seq.*

² Newton Friend, *Text Book of Inorganic Chemistry*, Vol. VI, Part II. (Prideaux), 130 *et seq.*

³ Smits and Rutgers, *J.C.S.*, 1924, 125, 2873.

⁴ *The Theory of Allotropy*, translated by Smeath Thomas (Longmans).

mixtures, or, in at least one case, a homogeneous solution. On the other hand, Cohen has shown, without reference to any special theory, that a great many pure substances are mixtures of more or less metastable forms.

According to the literature, the following modifications exist :

A. Existence undoubted. (I.) The ordinary amorphous powder. (II.) A vitreous form.

B. Existence more or less doubtful. (III.) A crystalline form produced by distillation at comparatively low temperatures, say 350°.

(IV.) A second crystalline form produced from the vitreous by prolonged heating, and having a melting-point of 569°. (V.) A third crystalline form, stable above 570°, in the absence of the lower melting-form. If all these forms existed as homogeneous individuals, the vapour pressure-temperature diagram would presumably look something like Fig. 1, where the Roman numerals refer to the modifications in the order named above. Broken curves indicate metastability. We

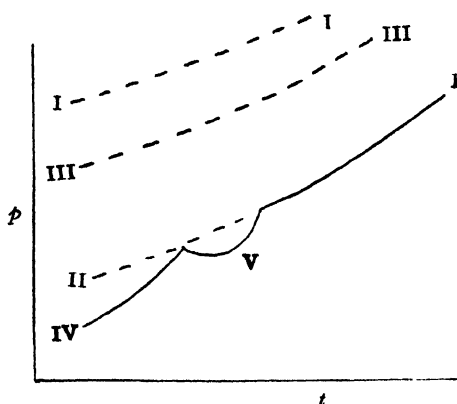


FIG. 1.

have investigated only forms I, II, and III, *i.e.*, the amorphous, the vitreous, and the low temperature crystalline.

Experimental Procedure.

The phosphorus pentoxide used was obtained from the Baker Chemical Company. It was a very light white powder, devoid of odour. It was impossible to purify this product by distillation in a current of oxygen, in view of the very large quantity, about eight pounds, used. Testing with silver nitrate revealed a slight reducing action; the product therefore contained traces of lower oxides. This fact has been borne in mind, and all the experimental methods are such as to discount any appreciable effect due to the presence of impurities.

It is shown by Smits ⁴ that, if a substance is a mixture the components of which are in equilibrium, solubility determinations will reveal no evidence of this if the equilibrium is established, as is usually the case, with very great velocity. If, however, the establishment of equilibrium is slowed down by anti-catalysts, such as intensive drying, the substance will show its heterogeneous character. Its behaviour with regard to solubility determinations will, however, differ from that of a mixture the components of which are not interconvertible; in the latter case saturation with both components will produce a solution of invariant composition (until one or the other of the components is extracted), followed by a jump to the solubility of the remaining pure form; in the former case there will be a progressive drift in solubility, with successive extractions, partly because we are passing along a series of mixed crystals, and partly because the re-establishment of equilibrium is not entirely inhibited: the drift will be from high solubility to progressively lower solubilities. Phosphorus pentoxide is an ideal substance for such measurements, because it is its own internal dryer. In other words, the effects of intensive drying (if, indeed,

those effects are real and fundamental), may be expected to be observed without the laborious technique of intensive drying.

Experimental.

Solubility determinations and diffusion experiments were carried out on each modification with a view, in the first place, to determining whether or not it was homogeneous. The solubility determinations were made by extracting in an all-glass Soxhlet apparatus over night. The solvent used was chloroform, washed with water, and dried over calcium chloride and phosphorus pentoxide, followed by distillation. The extract from the phosphorus pentoxide was placed in a thermostat at 26.9° , for six hours, and samples removed for analysis. A 25 c.c. sample was refluxed with water for ten minutes, cooled, and titrated with decinormal sodium hydroxide, using phenolphthalein as indicator. With this indicator, two-thirds of the molecule are neutralised.⁶

If the rate of diffusion of a solid into a solvent is considered, then, since the solvent in immediate contact with the solid is saturated, the rate of diffusion, other things being equal, will be proportional to the solution pressure of the solid. Forms with higher solution pressure, *i.e.* high diffusion coefficients, will be more metastable than forms with lower. The same form, if it be homogeneous, will always have the same diffusion coefficient, while, if it be heterogeneous, the diffusion coefficient will fall off with successive extractions. No attempt was made to evaluate the absolute value of the diffusion coefficient, but the following method was used for comparative measurements. A piece of burette tubing was sealed at one end. After heating to incipient redness to remove water adsorbed by the walls, a fragment of the modification in question was dropped in and 25 c.c. of dry chloroform poured in; 4 c.c. of distilled water were then run in on top. The heights of the columns were, chloroform, 13 cms.; water 2 cms. A pair of platinised conductivity electrodes were fixed in a constant position, about the centre of the water layer. The whole apparatus was kept in the thermostat. Observations of conductivity were made immediately after setting up the apparatus and at intervals of time. The conductivity increased steadily as the phosphorus pentoxide diffused through the chloroform and united with the water to form an electrolyte.*

A diffusion experiment was allowed to continue for a period of time ranging from 24 to 100 hours, depending on the velocity of diffusion. The aqueous layer was then removed and 4 c.c. of fresh distilled water introduced. In this way the sample was subjected to successive extractions. Since successive extractions of amorphous phosphorus pentoxide yielded steadily decreasing values for the velocity of diffusion, it was thought advisable to test the apparatus on an entirely different substance. For this purpose we chose arsenic trioxide; it yielded similar, although less strongly marked, results. On reflection, however, it seems to us by no means improbable that amorphous arsenic trioxide is also, in view of its mode of formation, a metastable mixture. This conclusion was borne out by solubility determinations on arsenic trioxide in chloroform, when the solubility also fell with successive extractions. The best test of the applicability of the method lies in the experiments on vitreous phosphorus pentoxide, which, provided it has been heated for a sufficient length of time in its preparation, seems to be the most stable form, and to be homo-

⁶ Sutton, *Volumetric Analysis*, 11th edition, p. 120.

* One obvious objection should be dealt with here. It may be said that what is measured is merely the rate of diffusion of water through chloroform, followed by the backward diffusion of acids of phosphorus through chloroform. The answer to this is that the apparatus gives results which are only to be interpreted on the basis of the diffusion of phosphorus pentoxide being the predominating phenomena; in other words, the solution pressure, or solubility, of phosphorus pentoxide in chloroform is much greater than that of water.

geneous. The values for velocity of diffusion in this case were low, and independent of the number of extractions.

The density of each allotrope was determined in a specific gravity bottle, having a capacity of 31.15 c.c. at 4°; *m*-Xylol was used as the inert liquid. In view of the smallness of the samples used (from 6 to 12 grams) the densities are only given to the third decimal. It is a common observation that the most stable form has the highest density, and conversely, but this is not thermodynamically necessary, as witness the density of stable ice, in relation to metastable water.

Ordinary Amorphous Phosphorus Pentoxide.

A compressed pellet of the phosphorus pentoxide weighing about 1 gram

Temp. = 26.9°.

No. of Extraction.	Sol. in Grams Per 100 gms. CHCl ₃ .
1	0.103
2	0.095
3	0.089
4	0.055
5	0.034
(1)	0.005

only was extracted.* It was, of course, impossible to use extraction thimbles, since cellulose is attacked by phosphorus pentoxide, and even glass wool is inadvisable, since it may contain adsorbed water. In this way the figures opposite for solubility were obtained.

Amorphous phosphorus pentoxide shows the behaviour of a mixture. It is not very likely that the initial high values are due to impurity, in view of the behaviour of the large quantity in respect to solubility. That the continued fall-off is due to impurity is impossible, since it must have been extracted in

the early extractions. The final low value may be due to the pellet having entirely disappeared. The measurements were repeated, using the phosphorus pentoxide in the form of a loose powder. The figures below were obtained.

The initial high value may be a particle size effect, or it may be due to some solid being carried over in the syphoning.†

Since the results of the diffusion experiments have no absolute value, the numerical results are not reproduced, neither are the plots of the figures, except in the first case, by way of example (Fig. 2). Instead of this we have tabulated the values of dc/dt (increase in conductivity in mhos per hour) for each extraction. Since the concentration of phosphorus pentoxide is constant at both ends of the chloroform layer (zero at the water end), the curve expressing increase of conductivity as a function of time should be a straight line of constant slope if the substance is homogeneous. Where the curve is not a straight line, we have given a mean value of dc/dt for each extraction.

The dc/dt values corresponding to Fig. 2, and to a repeat run on a fresh sample are given in the table on opposite page.

Both samples show the behaviour of a mixture, the differences in corresponding values of the coefficients are due to a difference in the area

Temp. = 26.9°.

No. of Extraction.	Sol. in Grams Per 100 gms. CHCl ₃ .
1	0.396
2	0.064
3	0.062
4	0.021
5	0.022

* Solubility determinations were first carried out on a large quantity, about 50 gms. of the powder, packed tightly in the mantle of the Soxhlet apparatus. With so large a quantity of the powder, a constant value for the solubility, 0.103 grams per 100 grams chloroform, was obtained, independent of the number of extractions. Owing to the small solubility of the pentoxide in chloroform, this would be the behaviour in any case, since successive extractions would only alter the composition of the residual pentoxide inappreciably.

† But see the solubility of the crystalline variety.

of cross-section of the pellets used; they are, however, of the same order of magnitude.

The density of the untreated powder was determined as previously described. Our figure is $d_4^{26.9} = 2.291$. Landolt-Börnstein⁶ gives $d = 2.387$ (temperature not stated). Our figure may be low, since it is difficult to free the fine powder entirely from air. On the other hand, for

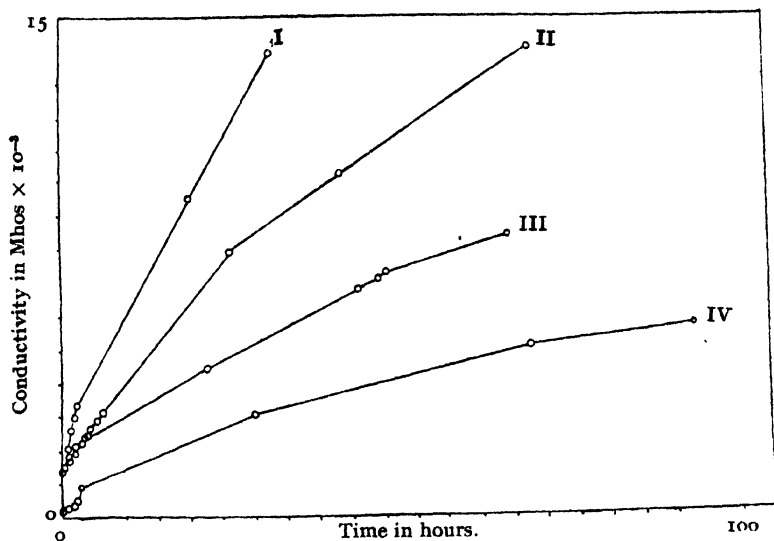


FIG. 2.—The Roman numerals refer to successive extractions.

such a mixture as amorphous phosphorus pentoxide undoubtedly is, the density is likely to depend very much on the method of preparation.

It was observed that on adding chloroform to the amorphous powder an immediate coagulation resulted. In view of the well-known work of Cohen on the stabilising effect of treatment with a liquid in which the substance is slightly soluble, the following experiment was carried out.

The amorphous powder was refluxed for 24 hours with chloroform and the chloroform then removed by distillation. The resulting product had a density of $d_4^{26.9} = 2.253$. Hence stabilisation had not resulted, despite the apparent change in appearance.

With a view to determining at what temperature change of state sets in, a hard glass test-tube was packed with the compressed powder and heated in an electric furnace at a constant rate. The tube carried a thermocouple and an exit to the suction pump. Temperature readings were taken every half-minute. Conversion to a more stable form is accompanied by evolution of heat, in this case probably small in amount, and evaporation by adsorption of heat. In all these experiments, we observed

	Extraction No.	$dc/dt \times 10^4$ in Mhos Per Hour.
1st Sample	1	3.50
	2	1.41
	3	0.74
	4	0.51
2nd Sample	1	0.75
	2	0.42
	3	0.126
	4	0.083

⁶ Landolt-Börnstein, *Physikalisch-chemische Tabellen*, 5th edition (1923), p. 305.

a pronounced lag in the heating curve, in the neighbourhood of 350° . Subsequent examination of the tubes showed that distillation had taken place, the pentoxide having been displaced several centimetres to a colder region of the tube. In this process, a stratification had taken place, which is of interest in the light of subsequent work. In the hottest zone was a highly crystalline deposit, shading off with falling temperature into a chalk-like mass, on top of which was the usual fine distilled powder. Apparently at 350° the amorphous form undergoes two processes, (1) its vapour pressure is sufficiently high to permit of free distillation (under reduced pressure), and (2), conversion to the (presumably) more stable crystalline form sets in.

The chalky form mentioned above was submitted to examination, in case it should prove to be a new modification. It had a density of $d_4^{26.9} = 2.317$, and a solubility of 0.099 gram per 100 grams chloroform on a first extraction. It appears to be the ordinary amorphous powder, agglomerated. Further experiments on heating the amorphous form are described under vitreous and crystalline respectively.

The Vitreous Form.

This form was prepared by heating the amorphous powder for three weeks in a sealed tube in an electric furnace at 450° . The time of heating is important, since subsequent work indicates that a shorter time of heating gives rise to a heterogeneous product. The product as obtained above was a clear transparent glass.

The graphs of the diffusion experiment gave parallel straight lines of small slope. The data are :—

Extraction No.	$dc/dt \times 10^4$ in Mhos Per Hour.
1	0.050
2	0.045
3	0.051
4	0.059

The solubility determination gave

1st Extraction. Solubility at $26.90^{\circ} = 0.0015^{\circ}$ gm./100 gm. CHCl_3 .

2nd Extraction. Solubility at $26.90^{\circ} = 0.0015^{\circ}$ gm./100 gm. CHCl_3 .

The density was found to be $d_4^{26.9} = 2.737$, i.e., 19 per cent. more dense than the amorphous form. This fact, taken in conjunction with the low, and constant diffusion velocities and solubilities, indicates that vitreous phosphorus pentoxide is homogeneous and more stable than the amorphous variety, indeed, than any variety we have studied.

The Low Temperature Crystalline Variety.

By this name, we mean the crystalline variety produced by heating the amorphous form at any temperature between 350° and 600° , provided the heating be not carried on too long. Prolonged heating results in the formation of vitreous. We have not succeeded in obtaining a pure preparation, nor do we believe it is possible to obtain one, because at the temperature at which the amorphous form begins to form the more stable crystalline, the crystalline is being transformed into the still more stable vitreous. That the vitreous is not formed directly from the amorphous results from the following experiment. A hard glass tube was packed tightly with the amorphous form, sealed and heated in an electric tube furnace at 550° for 48 hours. On opening the cold tube, which had been horizontal during the heating, it presented a peculiar appearance. The cross-section of the tube contained a honey-comb-like mass of crystalline variety, while on a dead level in the lower part of the tube was a layer of vitreous. This "vitreous," although glassy, was dazzlingly white. When examined by the usual methods it gave the following results. It had a density, $d_4^{26.9} = 2.195$, lower than

any other form of phosphorus pentoxide. This value is the mean of two determinations, on large quantities of substance, the individual values being 2.183 and 2.207. We conclude from this that this apparent vitreous is really a true solution (together with a certain amount of suspension) of either crystalline or amorphous in vitreous, the process of solution being accompanied by volume expansion. On prolonged heating no doubt the dissolved form is slowly converted into vitreous, so that the final product is one chemical individual. If this view is correct, it means that between the different allotropes of phosphorus pentoxide there must be a pronounced chemical, or at least physical, difference, *i.e.*, that the structural units must be vastly different, a view which receives support in the case of the stable vitreous, from the extreme slowness with which it is formed.

The structure assigned to this white vitreous form (*viz.*, that it is a solution of a less stable form in true vitreous, together with some mechanically intermingled particles of less stable form) is borne out by the results of the diffusion experiments. The first, third and fourth extractions yielded strictly parallel curves with a slope, $dc/dt \times 10^4$, of 0.062, that is, of the same order of magnitude as the stable vitreous. The second extraction, however, gave a rapidly ascending curve, having $dc/dt \times 10^4 = 1.00$, about the slope of the amorphous in an early extraction. The three parallel curves of small slope represent the solution pressure of the homogeneous solution, while the steep curve is due to the uncovering, by the act of dissolving of some suspended particles of amorphous (or possibly crystalline). Successive solubility determinations showed the same behaviour, for example, the first extraction gave a solubility of 0.0148 gram per 100 grams chloroform, the second of 0.0425 gram.

Returning to the crystalline form, we have already indicated that this, despite its highly crystalline appearance, must be more or less contaminated with amorphous and with vitreous. We should therefore expect it to behave, with respect to successive extractions, like a sample of amorphous, and this is what we have found. The density varied with the preparation, but, as a somewhat doubtful mean value, we give $d_4^{26.9} = 2.420$, slightly denser than the amorphous form.

The diffusion experiments yielded the above results.

One would expect the first extraction to yield the highest value, but it is very probable that the preparation is covered with a thin skin of partially vitrified material. For the rest the coefficients show the falling value characteristic of a mixture and are of the same order of magnitude as those of the amorphous. Solubility determinations gave (at 26.9°) (see table below).

We are indebted to Dr. G. M. Brownell, of the Geology Department, for an examination of the crystalline preparation in polarised light. He reports as follows: "The substance is anisotropic but contains amorphous or isometric matter. It is probably monoclinic or triclinic; extinction 45°; refractive index (mean for white light) < 1.485 , > 1.470 .

We have not been able to obtain either of the high temperature crystalline forms indicated in the literature,

but it is possible we did not continue heating for a sufficient time at the higher temperatures.

Extraction No.	$dc/dt \times 10^4$ in Mhos Per Hour.
1	1.08
2	1.95
3	0.475

No. of Extraction.	Solubility in Grams Per 100 Grams CHCl_3 .
1	0.215
2	0.143
3	0.0375
4	0.0137

Summary.

1. The densities, solution tensions, and solubilities of amorphous, vitreous, and one crystalline form of phosphorus pentoxide have been investigated.

2. Of the above three, the only homogeneous form is the vitreous, and this is the most stable, since it has the lowest solubility, and the highest density.

3. It is suggested that as vitreous forms from amorphous, a true solution of amorphous in vitreous is formed as an intermediate product. The properties of this solution have been studied. It is pointed out that if the two allotropes are sufficiently stable to form a true solution, their structural units must be very different.

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THE EFFECT OF OXIDISING AGENTS ON NICKEL DEPOSITION. II. CHROMIC ACID.

BY A. W. HOTHERSALL AND R. A. F. HAMMOND.*

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In a previous study of the effect of chromic acid on nickel deposition,¹ it was found that even in very small amounts, chromic acid caused a marked reduction in cathode efficiency. With increasing concentrations a tendency was observed for bare patches to appear on the cathodes and finally no deposit at all was formed. The solution buffered with ammonium sulphate was more sensitive to the effects of chromic acid additions than that buffered with boric acid. With different basis metals, there was a considerable difference in cathode efficiency during the early stages of deposition. Thus, the cathode efficiency was relatively high with copper and amalgamated copper, but very low with nickel, tin, lead, platinum and steel cathodes.

The present investigation has been carried out partly to provide an explanation of these results and in particular to compare the action of chromic acid with that of nitrate and hydrogen peroxide.²

Experimental Procedure.

The effects of chromic acid additions upon the cathode efficiency, the appearance of the deposits, the cathode potential, and the rate of gas discharge at the cathode were determined, using the methods previously described.² Nickel solution NSB. KC† was used, the composition being NiSO_4 , 7H₂O, 240; H₂BO₃, 30; KCl, 19 grammes per litre. The concentration of chromic acid present in the nickel solution was determined by

* The work described in this paper forms part of a programme of research on the electrodeposition of metals which is being carried out at the Research Department, Woolwich, with the aid of funds provided initially by the D.S.I.R. and later by the B.N.F.M.R.A.

¹ D. J. Macnaughtan and R. A. F. Hammond, *Trans. Faraday Soc.*, 1930, **26**, 481.

² A. W. Hothersall and R. A. F. Hammond, *ibid.*, 1934, **30**, 1079

† Solution "N" in previous report.¹

analysis before and after each experiment, using the diphenyl carbazide colorimetric method.

A current density of 1.2 amps./sq. dm. (11 amps./sq. ft.) and a temperature of 35° C. were used, except where otherwise stated.

Results.

Cathode Efficiency.

The results of the cathode efficiency determination are given in Fig. 1 in which, for convenience of comparison, a graph showing the effect of hydrogen peroxide and of nitrate additions is also reproduced. The concentration scales are proportional to the respective oxidising powers of the three addition agents to provide a direct comparison of their potential depolarising actions (1 g. $\text{NO}_3 \equiv 2.2$ g. $\text{H}_2\text{O}_2 \equiv 4.4$ g. CrO_3). The cathode

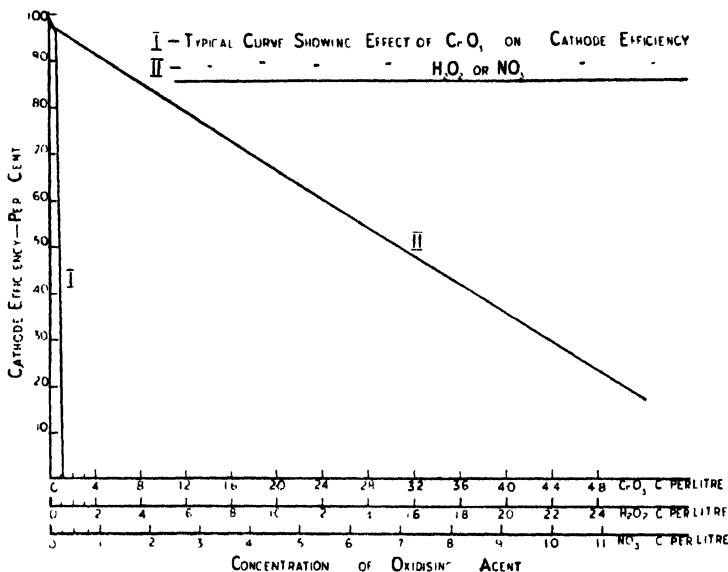


FIG. 1.—Comparative effects of I chromic acid and II hydrogen peroxide or nitrate upon cathode efficiency.

efficiency results of the present investigation agreed almost exactly with those described in the previous report.¹

The effect of solution p_{H} on the cathode efficiency in the presence of chromic acid was determined; the results which are summarised in Table I. show that a given concentration of chromic acid produces a greater reduction in efficiency at high than at low p_{H} .

Surface Appearance of Deposits.

The effect of chromic acid additions in increasing the lustrous appearance of the deposit, described in the previous report,¹ has been confirmed in the present investigation. It has further been found that the deposit is rendered considerably more lustrous in high than in low p_{H} solutions with a given concentration of chromic acid.

The deposits were slightly pitted in the absence of chromic acid. Small additions of CrO_3 had no effect in reducing the amount of pitting whilst concentration sufficient to render the deposits mirror-bright in appearance, led to a marked increase in the number of pits.

TABLE I.—THE EFFECT OF SOLUTION p_H ON THE CATHODE EFFICIENCY IN THE PRESENCE OF CHROMIC ACID.

Solution, NSB. KC.

Temperature, $35^\circ \pm 1^\circ$ C.

Current Density, 1.2 amps./sq. dm. (11 amps./sq. ft.).

p_{H_q} *	5'9.	5'6.	5'2.	4'9.	3'9.	3'1.
Cathode efficiency per cent. CrO_3 concentration <i>nil</i> .	99.3	99.4	99.4	99.35	99.2	98.3
Cathode efficiency per cent. CrO_3 concentration 0.073 g./l.	59.0	88.6	91.7	91.2	91.7	90.8

* A subscript q indicates that the p_H value was determined with the quinhydrone electrode.

Gas Discharge at the Cathode.

With increase in the concentration of chromic acid, the rate of gas discharge first decreased slightly (up to 0.03 g. CrO_3 per litre), and then rapidly

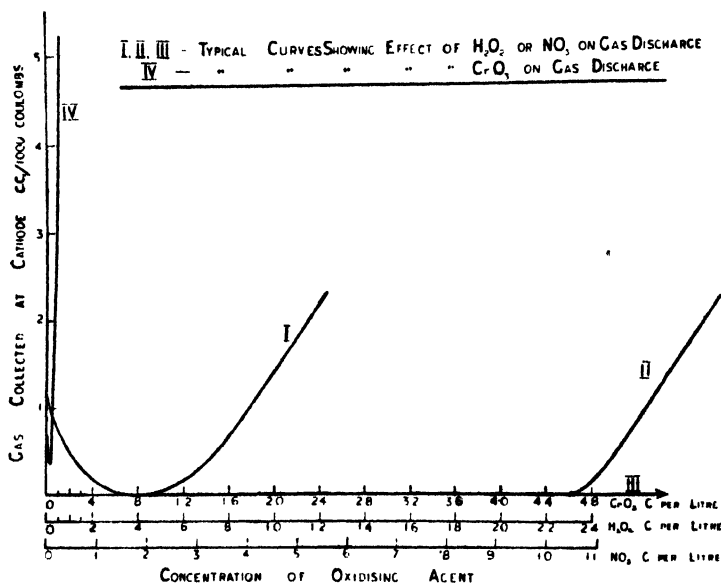


FIG. 2.—Comparative effects of hydrogen peroxide or nitrate (Curves I, II and III) and of chromic acid (Curve IV), upon gas discharge at the cathode.

increased. At no concentration was gas discharge inhibited as was observed with hydrogen peroxide and nitrate additions.² The results of a typical experiment are given in Fig. 2, together with a typical curve for H_2O_2 and NO additions, the ordinates being arranged on the basis of equivalent oxidising power for the purpose of comparison.

Cathode Potential.

The cathode potential was found to increase only slightly in the presence of small concentrations of chromic acid. With higher concentrations, a

marked rise in potential was observed; this rise coincided with a rapid increase in the rate of gas evolution. The results are shown in Table II.

TABLE II.—EFFECT OF CHROMIC ACID ON CATHODE POTENTIAL

Solution, NSB. KC at p_H 3.0.

Temperature, $35 \pm 1^\circ \text{C}$.

Current Density, 2.4 amps./sq. dm. (22 amps./sq. ft.)

Concentration—g. CrO_3 /l.	Nil.	0.04.	0.08.	0.11.	0.15.
Cathode potential—volts E_H	— .59	— .59	— .60	— .62	— .63 rising rapidly to — 1.08
Remarks	Slight gas evolution.				Vigorous gas evolution

Cathodic Reduction of Chromic Acid.

Analytical determinations showed that in all experiments some chromic acid had been reduced. It was, however, found that, in any one experiment, the amount of chromic acid reduced was always much less than equivalent to the quantity of hydrogen ions discharged. The ratios of the observed quantity of chromic acid reduced to that calculated from the cathode efficiency result varied from 1 : 2.2 to 1 : 57; the ratio appeared to increase with the concentration of chromic acid. This was confirmed by special experiments in which electrolysis was carried out in two cells, connected in series, each containing two litres of the same nickel solution but with different concentrations of chromic acid; the amounts of CrO_3 reduced in each cell were determined by analysis and compared with those theoretically possible, as calculated from the cathode efficiencies.

The results of two experiments are shown in Table III. :—

TABLE III.—EFFECT OF CHROMIC ACID CONCENTRATION ON THE AMOUNT OF REDUCTION AT THE CATHODE FACE.

Solution, NSB. KC at p_H 2.8.

Temperature, $35^\circ \pm 1^\circ \text{C}$.

Current Density, 1.2 amps./sq. dm. (11 amps./sq. ft.).

Time, five hours.

Experiment.	Concentration g. CrO_3 /litre.		Total CrO_3 Reduced g.	Cathode Efficiency Per Cent.	Ratio CrO_3 Reduced Actual CrO_3 Reduced Theoretical.	Remarks.
	Before Run.	After Run.				
1	.062	.031	.062	76.1	1 : 9	Low CrO_3 concentration.
2	.053	.025	.056	94.7	1 : 2.2	
1a	.193	.172	.042	6.1	1 : 52	High CrO_3 concentration.
2a	.243	.223	.040	1.2	1 : 57	

Discussion of Results.

The effect of nitrate and hydrogen peroxide in causing a linear decrease in cathode efficiency of nickel deposition was attributed to depolarisation,² the amount of oxidising agent reduced corresponding to the quantity calculated from the cathode efficiency. Although some depolarisation resulted from the addition of chromic acid, as indicated by reduction of Cr^{VI} to Cr^{III} , the amount of chromic acid actually reduced was small compared with the calculated quantity equivalent to the decreased cathode efficiency; furthermore, gas discharge was not appreciably diminished in the presence of chromic acid. Thus, the effects produced by chromic acid on nickel deposition can only be indirectly, and to a small degree, connected with depolarisation.

As described in the previous report, very small concentrations of chromic acid produced a relatively slight reduction in current efficiency, the current efficiency/concentration curve being approximately linear as with nitrate and hydrogen peroxide. With increase in chromic acid concentration above a critical value, the curve bent steeply and the efficiency rapidly fell to, and remained at, zero.

The current efficiency/concentration curve thus appears to suggest two distinct types of cathode reaction: (1) in which nickel is being deposited at high but gradually falling efficiency, the process being accompanied by some cathode depolarisation, and (2) in which hydrogen only is discharged. The steeply falling middle section of the curve corresponds to an intermediate condition in which both types of reaction are occurring simultaneously on different parts of the cathode.

The first process may be explained by the action of chromic acid in assisting the precipitation of basic nickel compounds at the cathode face, whilst the second appears to result from the formation of a selectively permeable film on the cathode surface by chemical interaction between the chromic acid and the cathode metal.

1. Effect of Chromic Acid on Precipitation at the Cathode Face.

In all experiments with high p_{H} solutions containing chromic acid, it was found that the bath became increasingly turbid as electrolysis was continued. A precipitate produced in this way in solution NSB. KC at p_{H} 5.9, was filtered off, washed, dried at 100°C ., and analysed. The result of the analysis was as follows:—

NiO	.	.	54.2	per cent.
B_2O_3	.	.	12.9	" "
SO_4	.	.	9.9	" "
Cr_2O_3	.	.	8.6	" "
CrO_3	.	.	0.7	" "
H_2O (combined)			16.1	" "

The high ratio of trivalent to hexavalent chromium in the precipitate is evidence of cathodic reduction of chromic acid. The normal increase in OH^{\cdot} concentration at the cathode surface is somewhat augmented by the cathode depolarisation, and hydrolysis of the reduced chromium salt is thus accelerated. It was established in independent experiments, that the precipitates which form when chromic sulphate is added to filtered nickel solutions at p_{H} values in excess of about 5, contain, after thorough washing, a large percentage of nickel. This is in accordance with the high concentration of nickel shown in the above analysis. It is thus evident that reduction of the nickel ion concentration in the catholyte will result, which may explain why the fall in cathode efficiency in this range exceeds the amount which would be anticipated from the quantity of chromic acid reduced.

It was also found that precipitates containing both Cr and Ni were formed when chromic acid was added to filtered nickel solutions, either NSB . KC or NSA . KC, when the p_H exceeded a critical value of p_H 5.2, and p_H 6.0, respectively. It is therefore possible that the depletion of nickel ions in the vicinity of the cathode was further assisted in this way; the presence of hexavalent chromium in the precipitate supports this suggestion.

2. Complete Inhibition of Nickel Deposition.

Complete inhibition of nickel deposition has been found to occur over a wide range of solution p_H and in solutions of different compositions. It was found in certain experiments that a given concentration of chromic acid produced a greater effect at low than at high current densities. For example, at current densities of 1.2 and 1.5 amps./dm.² in solution NSB . KC at p_H 5.9, containing 0.09 g. CrO₃/litre, relatively little gas was evolved and the cathode potential was little different from normal. Violent agitation of the solution produced no apparent change in the cathode process. On reducing the current density to 0.4 amp./dm.², however, and agitating the solution, a vigorous evolution of gas set in, a high cathode potential being recorded. This condition persisted after the agitation had ceased and when the current density was restored to 1.2 amps./dm.².

In further experiments, sheet copper cathodes bent into the form of letter "S" were used in solution NSB . KC at p_H 5.9, containing chromic acid. With a suitable current density and concentration of chromic acid, deposit formed only on the protruding portions of the cathode whilst the receding parts remained completely bare. This effect was obtained at a current density of 0.8 amps./dm.² in the presence of 0.11 g. CrO₃/l. and at 1.6 amps./dm.² with 0.14 g. CrO₃/l. When the current density was reduced the cathodes remained completely bare, whilst at higher values continuous deposits were produced. The effect was observed irrespective of whether the axis of the bends was in a vertical or a horizontal position.

The results of the above experiments suggested that the complete inhibition of nickel deposition was due to chemical interaction between the cathode metal and chromic acid, with the resulting formation of a selectively permeable film on the surface of the metal allowing the passage of H⁺ but not Ni²⁺ ions. The results obtained in the following additional experiments tend to confirm this view.

(a) Copper cathodes coated with freshly deposited nickel were dipped for one minute into either solution NSB . KC or NSA . KC, to which had been added varying concentrations of chromic acid. The cathodes were then thoroughly rinsed and immediately placed into a nickel depositing bath free from chromic acid. When the concentration of CrO₃ in the first solution exceeded a critical value, showers of bubbles were formed when deposition was started, and an abnormally high cathode potential was recorded. At concentrations below the critical value, the cathodes were quiescent and the cathode potential was normal. The critical concentration was found to be markedly higher in the boric acid solution than in the ammonium salt solution; this is in agreement with the observed greater sensitivity of the latter solution to CrO₃ additions.

(b) In another series of experiments a concentration of 0.07 g. CrO₃/litre was added to solution NSB . KC at p_H 5.9. This was not sufficient to cause vigorous gas evolution or appreciable change in cathode potential from the normal value (— 0.6 volt E_H). On remarking the circuit after breaking it for thirty seconds, there was a vigorous discharge of gas at the cathode which was maintained and the potential rose to an abnormally high value (— 0.85 volt E_H). It was found that dipping the cathode momentarily into 10 per cent. sulphuric acid restored it to the normal condition, and after rinsing, nickel deposition again took place at normal potential and without marked gas evolution. This sequence could be repeated at will. Stirring

the solution was found to reduce materially the time of current interruption necessary to produce the effect

(c) Deposition was carried out in a nickel solution containing chromic acid in amount insufficient to cause excessive discharge of gas. When a stream of the electrolyte was blown vigorously on to the centre of the cathode surface from a jet, a change in the appearance of the deposit was immediately observed over the area affected. After deposition for seventeen hours, the portions of the cathode surrounding the affected area were thickly coated with a "burnt" and exfoliated nickel deposit. The central zone, however, remained almost unchanged in appearance throughout and it appeared that nickel deposition over this area had ceased from the moment at which the jet of solution impinged on the cathode surface. This suggested the presence of a film over the surface of the cathode metal on the affected area.

Visual evidence of local film formation as a result of stirring the solution during deposition was obtained by observing a strongly illuminated cathode. The film commenced to form on the cathode where the agitation was most violent and gradually spread in the direction of stirring. Reversing the direction of stirring caused the film to spread in the opposite direction. A deposit showing surface markings typical of this effect is shown in Fig. 3.

(d) Chromic Acid Additions to Copper Solutions.

The above hypothesis of film formation by chemical attack of the cathode metal appears to be confirmed by the results of experiments in which chromic acid additions were made to copper sulphate solutions.

An approximately neutral solution of copper sulphate containing 250 grammes of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ per litre was prepared by boiling with basic copper carbonate, cooling and filtering. This solution was electrolysed using copper cathodes at a cathode current density of 1.2 amps/sq dm (11 amps/sq ft) both in the absence and in the presence of chromic acid. In the absence of CrO_3 , the deposits though somewhat dark in colour were continuous. As the CrO_3 content was increased, a progressively larger proportion of the cathode surface remained uncoated, the deposit being formed in vertical streaks up the cathode and at the sites of scratches on the basis-metal. This effect was very pronounced at a concentration of 1.1 g CrO_3 per litre, and typical deposits are illustrated in Fig. 4. A cathode efficiency determination at this concentration gave a result of 10.4 per cent, the high value presumably resulting from the high local current density which caused the deposit to be somewhat basic. It appears that deposition took place only at weak points in a surface film which was formed when the copper cathode was first placed into the solution.

Similar results were obtained in a weakly acid solution of copper sulphate containing boric acid, but in a copper sulphate solution containing 50 grams per litre of free sulphuric acid, the appearance of the deposits was unaffected by chromic acid in concentrations up to 1.5 g CrO_3 per litre.

The Influence of the Basis-Metal.

In the previous investigation it was found that the cathode efficiency during the first ten minutes of deposition varied from about 1 per cent (platinum, tin, lead and steel), to 90 per cent (copper and amalgamated copper), in solution NSB KC at p_H 5.2, containing 0.11 g CrO_3 per litre. The results of the present work suggest that these differences arise from the varying capacities of these metals to form selectively permeable films by chemical interaction with chromic acid during the initial stages of electrolysis and also that the behaviour of a given metal depends on the conditions of the experiment.

Whilst it would not be anticipated that platinum would react with chromic acid, it was nevertheless found that if a platinum cathode was



← Solution level.

FIG. 3.—Nickel deposit showing surface markings suggesting the presence of a film on the cathode

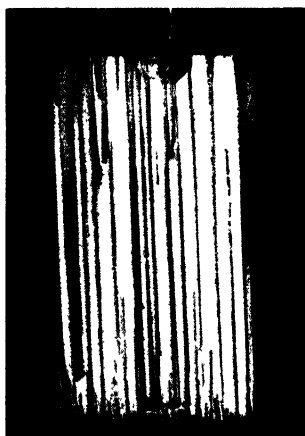


FIG. 4. —Typical copper deposits produced in a neutral copper sulphate solution containing 1.1 g. CrO_3 per litre. Deposit confined to isolated streaks and spots.

[To face page 1580.

allowed to remain for one minute in the solution with no current passing, little or no nickel was deposited when the circuit was completed, whereas in the same conditions, immersion of the cathode with the circuit closed resulted in deposition of nickel at high efficiency. These results are concordant with observations by Müller³ on the difference in behaviour of platinum and carbon cathodes in the deposition of chromium from chromic acid solution, and confirm Liebreich's suggestion⁴ that interaction of the solution with the metal of the cathode may play a prominent part in the cathode process.

Note on the Behaviour of Ignited Platinum.

It was found that ignition of a platinum foil cathode in a bunsen flame produced a marked effect upon its behaviour during electrolysis in NSB . KC solution at p_H 5.9, containing 0.06 g. CrO_3 per litre. When the foil was cleaned in acid, rinsed, ignited, and again rinsed in distilled water prior to immersion in the solution, zero cathode efficiency was recorded. After a similar cleaning treatment but omitting the ignition, nickel was deposited at relatively high efficiency. The difference may have resulted from the presence on the cathode after ignition of a deposit of finely divided platinum,⁵ which would be expected to react with, or adsorb, chromic acid more rapidly; the lower hydrogen overvoltage of such a surface might also be a contributory factor.

Summary and Conclusions.

A previous investigation of the effect of chromic acid on the cathode efficiency of nickel deposition and on the appearance of the deposit has been extended to provide an explanation of the results and to compare the behaviour of chromic acid with that of nitrate and hydrogen peroxide.

Increasing concentrations of chromic acid were found to cause a marked decrease in cathode efficiency and to render the deposits first bright, then exfoliated, "burnt," and finally to result in the complete inhibition of nickel deposition. With a given concentration of chromic acid, a greater effect was produced at high than at low p_H .

Low concentrations of chromic acid were found to produce little if any diminution in gas discharge at the cathode, whilst amounts in excess of 0.03 g. CrO_3 per litre caused a rapid increase in the rate of gas evolution. The presence of chromic acid did not diminish pitting.

A rapid rise in potential accompanied by vigorous gas discharge, occurred when the chromic acid concentration reached a critical value. In solutions containing somewhat less than the critical concentration, this effect could be induced by interrupting the current for a short time, or at low current densities by merely stirring the solution.

Analytical determinations of CrO_3 concentration showed that the amount of cathodic reduction was in all experiments considerably less than sufficient to correspond with the quantity of hydrogen ions discharged; with high concentrations of chromic acid, this discrepancy was accentuated. Thus, unlike nitrate and hydrogen peroxide, the effects produced by chromic acid on nickel deposition can only be connected indirectly and to a small degree with depolarisation of hydrogen.

The results suggested that chromic acid may function in two ways: (1) With low concentrations, initial depolarisation results in precipitation of basic nickel compounds containing chromium at the cathode face, the nickel ion concentration being thereby depleted. Hydrogen ion discharge and reduced cathode efficiency are thus favoured. (2) With higher concentrations, chromic acid interacts chemically with the cathode metal

³ E. Müller, *ibid.*, 1935, 31, 1194.

⁴ E. Liebreich, *ibid.*, 1935, 31, 1188.

⁵ J. H. T. Roberts, *Phil. Mag.*, 1913, 25, 270.

with the formation of a selectively-permeable film on its surface; nickel deposition is completely inhibited as a result. With intermediate concentrations both of these effects may occur simultaneously.

The specific behaviour of different basis metals appears to result from their differing capacities to form surface films by interaction with chromic acid.

THE CONCEPTION OF A COMPLEX VISCOSITY AND ITS APPLICATION TO DIELECTRICS.

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1. Introduction.

During recent years, the variation with frequency of the damping of vibrating systems has been noticed in three independent fields in physics. The first concerns the viscosity of that class of liquids which exhibits the phenomenon of structure-viscosity. This phenomenon was first observed by E. Hatschek¹ for colloidal solutions, and has since been investigated by others, including the author,² who succeeded in showing it for heavy oils. The apparent viscosity decreases with increasing mechanical stress, and, as W. Philippoff³ has shown, with increasing frequency of the motion.

The second field concerns the damping of vibrations and longitudinal waves in solids. J. H. C. Thompson⁴ has compared the values for the viscosity of metals obtained by the following authors: Hettwer⁵ (for very low frequencies of the order 10^{15}), Honda and Konno⁶ (for higher frequencies of the order 10^8), and S. L. Quimby⁷ (for ultrasonic frequencies of the order 10^3 , this value applying also to glass). There is an evident decrease with increasing frequency, even though the quantitative accuracy of these data may be somewhat open to criticism. The same result has been obtained for rubber by P. W. Bridgeman and H. M. Trueblood⁸ and recently by J. C. Eccles and J. H. C. Thompson⁹ for a restricted low frequency range.

The third field concerns dielectric losses in insulating materials. The losses in glass are, according to M. J. O. Strutt,¹⁰ due at least partly, to dipoles, and this fact requires a relatively low value of apparent viscosity. According to W. Jackson,¹¹ the viscosity of paraffin wax, as calculated from dielectric losses, is considerably lower than the static value. Though

¹ E. Hatschek, *Koll. Z.*, 1913, **13**, 88.

² A. Gemant, *Berl. Akad. Ber.*, 1932.

³ W. Philippoff, *Physik. Z.*, 1934, **35**, 884.

⁴ J. H. C. Thompson, *Phil. Trans.*, 1933, **231A**, 339.

⁵ Hettwer, *Wien. Ber.*, 1925, **134**, 51.

⁶ Honda and Konno, *Phil. Mag.*, 1921, **42**, 115.

⁷ S. L. Quimby, *Physic. Rev.*, 1925, **25**, 559.

⁸ I. B. Crandall, *Vibrating Systems and Sound*, London, 1927, p. III.

⁹ J. C. Eccles and J. H. C. Thompson, *Proc. Roy. Soc.*, 1935, **148A**, 171.

¹⁰ M. J. O. Strutt, *Arch. Elektrot.*, 1931, **25**, 715.

¹¹ W. Jackson, *Proc. Roy. Soc.*, 1935, **150A**, 197.

very little reliable data is available, the general characteristic seems to be the same as in the other two cases.

Only the first of these three domains (structure-viscosity of liquids) has been at all widely investigated, and a theoretical explanation is already available. H. Hencky¹² described the observed phenomena by assuming the Maxwellian conception¹³ to hold for these liquids. According to this conception, the stress F and strain S are related by the equation :

$$\frac{dS}{dt} = \frac{1}{E} \frac{dF}{dt} + \frac{F}{\eta} \quad . \quad . \quad . \quad . \quad (1)$$

where t = time, E = shear modulus of elasticity and η = viscosity. By using electrical analogies, this means that the current dS/dt is composed of two terms: one in phase with the voltage F (this being the current in a resistance η) and the other in phase quadrature, corresponding to the current in a capacitance $1/E$. An extended theory on this basis has been built up in the field of plasticity problems.¹⁴

The theory now to be developed is in some measure a generalisation of this Maxwellian conception which proved so useful for liquids exhibiting structure-viscosity. According to our idea,¹⁵ the viscosity should be replaced quite generally by a complex impedance, at least in all cases concerned with alternating molecular phenomena. This impedance may be termed the "complex viscosity," denoted by V , and its introduction in place of the real one, η , may lead to an explanation of the other two (*vis.*, the acoustical and electrical) effects. It would be attractive if these three phenomena, differing so widely, could be explained by one and the same theory. The name complex viscosity shows at once the main idea, just as one speaks of a complex A-C. conductivity of dielectrics, implying both the losses and the displacement current.

2. The Complex Viscosity.

Although it seems at first sight that the above assumption is merely formal, it has obviously a definite underlying physical meaning, *vis.* that the molecules are capable of motions of two kinds. They can be displaced elastically, but they may also undergo a change of position, *i.e.*, a viscous flow. Which of these two actually occurs, depends on the frequency. For a continuous stress the flow is viscous, whereas with increasing frequency it will tend more and more towards the elastic displacement. The change takes place near the frequency determined by the reciprocal of the time constant of elastic relaxation.

It is probable that the real physical structure cannot be depicted by a simple electrical circuit. However, an approximation is still possible. The simple parallel circuit of capacitance and resistance is not sufficient, since there is a certain damping even at the highest frequencies. The circuit shown in Fig. 1 is the simplest one which fulfils the condition of a finite damping even at these highest frequencies. R_0 is the steady state viscosity unit, C represents the reciprocal of the elasticity, and R the damping unit during elastic displacement. As Thompson⁴ points out,

¹² H. Hencky, *Ann. Physik*, 1929, **2**, 617.

¹³ J. C. Maxwell, *Phil. Mag.*, 1868, **35**, 133.

¹⁴ *First Report on Viscosity and Plasticity*, Academy of Sciences at Amsterdam, 1935, p. 21 and following.

¹⁵ A. Gemant, *Naturwiss.*, 1935, **23**, 406.

is, therefore, zero, or at least very small, which is the case for a liquid. Considering that the shear modulus of amorphous bodies like glass or resin increases distinctly with decreasing temperature, the curve relating C with temperature had to be assumed, to have the shape of the dotted line in Fig. 2. For the liquid, C is zero, as soon as solidification begins it jumps suddenly to a high value and subsequently decreases. No minimum of elasticity, corresponding to the maximum of C , has yet been detected in colloidal solutions.¹⁷

It is perhaps more logical to assume that the elasticity decreases continuously with increasing temperature (full line in Fig. 2), though the change is again not so large as that of R_0 . Since R_0 becomes small for the liquid, it is still possible for τ_0 to be very small, even though C remains finite.¹⁸ Moreover, since R is of the same order as R_0 for the liquid, there will not be any appreciable change in damping, whether the frequency is higher or lower than $1/\tau_0$. Again, experiment must decide which of these two possibilities is the more correct.

The following is an application of the theory to dielectric losses. The acoustic question will be treated elsewhere. At first the general equations will be derived.

3. The Mathematical Expression for V .

Accepting the circuit shown in Fig. 1 as the electric equivalent for the complex impedance, it can be expressed mathematically. We reduce the circuit to a resistance R' and capacitance C' in series. This means that in the general expression for the viscosity unit, namely $A - iB$, A is given by

$$A = R'$$

while

$$B = \frac{1}{\omega C'}$$

where ω is 2π times the frequency. The complex viscosity has therefore the general form :

$$V = R' - \frac{i}{\omega C'} \quad . \quad . \quad . \quad (3)$$

or replacing C' by $1/E'$,

$$V = R' - \frac{iE'}{\omega} \quad . \quad . \quad . \quad (4)$$

In computing the total impedance of the circuit and bringing it to the form (3), we get, after a simple calculation :

$$R' = \frac{R_0[1 + (R\omega C)^2][1 + R(R_0 + R)(\omega C)^2]}{[1 + R(R_0 + R)(\omega C)^2]^2 + (R_0\omega C)^2} \quad . \quad . \quad (5)$$

and

$$C' = \frac{[1 + R(R_0 + R)(\omega C)^2]^2 + (R_0\omega C)^2}{R_0^2\omega^2 C[1 + (R\omega C)^2]} \quad . \quad . \quad (6)$$

It can be seen that, for $\omega = 0$, R' assumes the value R_0 , whereas for $\omega = \infty$ it becomes $R_0 R / (R_0 + R)$. C' becomes infinite for $\omega = 0$, and $[(R_0 + R)/R_0]^2 C$ for $\omega = \infty$.

For most cases of interest

$$R_0 \gg R.$$

¹⁸ The same view was expressed by Mr. N. L. Yates-Fish, University College, Swansea, in a communication to the author.

The expressions may be simplified considerably, by neglecting R against R_0 . Introducing further τ_0 from (2) and writing:

$$\tau = RC \quad . \quad . \quad . \quad (7)$$

we get:

$$R' = R_0 \frac{1 + \tau\tau_0\omega^2}{1 + (\tau_0\omega)^2} \quad . \quad . \quad . \quad (8)$$

and

$$C' = C \frac{1 + (\tau_0\omega)^2}{(\tau_0\omega)^2} \quad . \quad . \quad . \quad (9)$$

or

$$E' = E \frac{(\tau_0\omega)^2}{1 + (\tau_0\omega)^2} \quad . \quad . \quad . \quad (10)$$

Equations (4), (8) and (10) are the general expression for the complex viscosity and may be used in any application.

The limiting case of a crystal ($R_0 = \infty$) means that $R' = R$ and $E' = E$ independent of frequency. The other limiting case, namely of a liquid, can be treated in two different ways, as stated above. If $E = \infty$ and consequently $\tau_0 = 0$, then $R' = R_0$ and $E' = 0$, as required. On the other hand E may be finite and R of the same order as R_0 . In this case equations (5) and (6) must be consulted. R' remains substantially unaltered during the whole frequency range, whereas $E' = 1/C'$ assumes finite values, but as they are rather low, they are probably of no great importance.

4. Dipole Rotation with Complex Viscosity.

The following should show the application of the theory to dipole rotation. The subject has already been treated by the author,¹⁹ but in a different manner. The treatment adopted there showed that Debye's theory holds also for amorphous solids, but left open the question as to the variation of viscosity with frequency. Introducing the complex viscosity it is possible to get a more positive answer to this question.

Equation (4) has to be introduced in the dipole theory. The last of Debye's complex equations is:²⁰

$$\epsilon = \frac{\frac{\epsilon_0}{\epsilon_0 + 2} + i\omega\tau_t \frac{\epsilon_\infty}{\epsilon_\infty + 2}}{\frac{1}{\epsilon_0 + 2} + i\omega\tau_t \frac{1}{\epsilon_\infty + 2}} \quad . \quad . \quad . \quad (11)$$

where ϵ is the complex dielectric constant, ϵ_0 and ϵ_∞ are the limiting values for D.C. and very high frequency and τ_t is the thermal time constant, namely $\zeta/2kT$.^{*} ζ is proportional to the viscosity, being $8\pi\eta r^3$ (r = radius of rotating molecule) and we replace it therefore by the corresponding complex value, V_r :

$$V_r = \zeta' - \frac{i\gamma'}{\omega} \quad . \quad . \quad . \quad (12)$$

¹⁹ A. Gemant, *Phil. Mag.*, 1935, **19**, 746.

²⁰ P. Debye, *Polar Molecules*, New York, 1929, § 19.

^{*} ζ = viscous resistance to rotating sphere, k = Boltzmann constant, T = absolute temperature.

Replacing R_0 by ζ_0 , R by ζ and E by γ , where γ is the corresponding elastic counterforce for a twisted rigid sphere, being :

$$\gamma = c \frac{E}{\eta_0} \zeta_0$$

(c = a numerical factor, probably unity), we thus have instead of (8) :

$$\zeta' = \zeta_0 \frac{1 + \tau \tau_0 \omega^2}{1 + (\tau_0 \omega)^2} \quad (8a)$$

and instead of (10) :

$$\gamma' = \gamma \frac{(\tau_0 \omega)^2}{1 + (\tau_0 \omega)^2} \quad (10a)$$

We get for τ_i :

$$\tau_i = \frac{\zeta'}{2kT} - i \frac{\gamma'}{2kT\omega}$$

or, denoting the real part by τ' and $\gamma'/2kT$ by λ :

$$\tau_i = \tau' - i \frac{\lambda}{\omega} \quad (12)$$

The real part, τ' , has the meaning of a time constant. Substituting (12) in (11) the real and imaginary parts may now be separated. It may be assumed for the sake of simplicity, that :

$$\frac{\epsilon_0 + 2}{\epsilon_\infty + 2} \sim 1$$

as is generally allowable. We get then for the real part ϵ' , *i.e.*, the real dielectric constant, approximately :

$$\epsilon' = \epsilon_\infty + \frac{1 + \lambda}{(1 + \lambda)^2 + (\omega \tau')^2} (\epsilon_0 - \epsilon_\infty) \quad (13)$$

The factor

$$k' = \frac{1 + \lambda}{(1 + \lambda)^2 + (\omega \tau')^2} \quad (13a)$$

is mainly of importance. The ratio of the imaginary and real parts is the loss angle $\tan \delta$:

$$\tan \delta = \frac{\omega \tau'}{(1 + \lambda)^2 + (\omega \tau')^2} \cdot \frac{\epsilon_0 - \epsilon_\infty}{\epsilon_0} \quad (14)$$

Again the factor

$$k'' = \frac{\omega \tau'}{(1 + \lambda)^2 + (\omega \tau')^2} \quad (14a)$$

is the interesting one.

On comparing (13) and (14) with the corresponding Debye-equations ($\lambda = 0$, $\tau' = \tau_i$) the following two differences are noticeable.

In the first place $(1 + \lambda)$ replaces 1, but this is only a minor alteration. Since equation (11) was used as starting equation, thermal agitation, represented by the term $2kT$ is the dominating moment, impeding the orientation of dipoles. Elastic restraint is therefore only a kind of correction term. Equations (13) and (14) are valid only so long, as

$$\lambda < 1,$$

or

$$\gamma' < 2kT \quad (15)$$

Consulting Fig. 2, and remembering that $\gamma = \frac{1}{C}$, we see, that the above equations are not valid for a low temperature range, in which the elastic forces outweigh thermal forces, *i.e.*, for the crystalline state. In any case, the rotational dipole theory is inapplicable to crystals. The theory put forward in this paragraph is valid for the transition state between liquids and crystals, the so-called vitreous state. In practice, a great number of insulating materials exist in such a vitreous phase.

The second, more important, alteration, compared with the original theory is the change of time constant with frequency. τ' is (according to equation (8a)) a function of ω . For low frequencies it is $\zeta_0/2kT$, decreases in a frequency range given by $1/\tau_0$, and finally stops at the value $\zeta/2kT$. This involves some characteristic features in the $\tan \delta$ -frequency curve.

5. Numerical Calculations.

(a) A somewhat frequent case with amorphous (or partly amorphous) solids is given by :

$$\tau_0 > 1.$$

This means that over all practical frequencies the damping is represented by the "high-frequency" term. Such is the case, perhaps, for waxes in the temperature range just below solidification, where there is a mixture of partly crystalline, partly glassy components.²¹ The only alteration in the $\tan \delta$ curve is now that the apparent viscosity is unconnected with the static value ζ_0 ; otherwise the behaviour is quite regular. This is in accord with the observations of Jackson.¹¹ The condition $\tau_0 > 1$ is roughly equivalent to values of the static viscosity :

$$\eta_0 > 10^8.$$

(b) If η_0 and correspondingly τ_0 is not so high, as is quite possible, we come to the more general case, in which the region of finite losses is

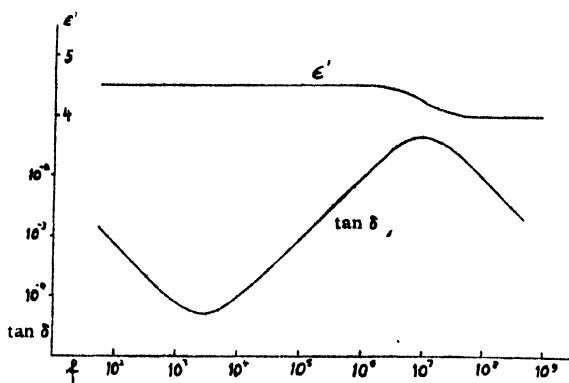


FIG. 23.—Dielectric constant and loss angle calculated ($\tau_0 = 10^{-1}$ sec.).

extended over a wider range of frequency; *i.e.*, the increase of ω in the argument ($\omega\tau'$) is counteracted by a corresponding decrease in τ' . This is an important point in the theory. Insulation losses are generally not so sharply restricted to a small range as the simple theory requires. This is due partly to several coexistent

dipole molecules, partly to an overlapping of different mechanisms. But partly it may be due to an extension of dipole rotation for the above reason.

²¹ A. Gemant, *Nature*, 1935, 135, 912.

Generally, there may be two maxima of loss angle corresponding to the time constants $\zeta_0/2kT$ and $\zeta/2kT$. A numerical calculation follows, in which $\zeta_0 = 10^{-15}$, $\eta_0 \sim 10^7$ and $\tau_0 = 10^{-1}$ sec. (Roughly: $\eta_0 \sim 10^{22} \zeta_0$.) The other data are: $2kT = 10^{-14}$, $\gamma = 10^{-14}$ (limiting case according to equation (15)) and $\zeta = 3 \cdot 10^{-22}$ (corresponding to $\eta \sim 3$). All these figures are in absolute units. Let us further assume $\epsilon_0 = 5$ and $\epsilon_\infty = 4$. τ_0 still being rather high, the first maximum will not be observable, there being only an initial decrease in $\tan \delta$. Fig. 3 shows the results of the calculation, namely ϵ' and $\tan \delta$ as a function of the frequency f from 50 to $5 \cdot 10^8$.

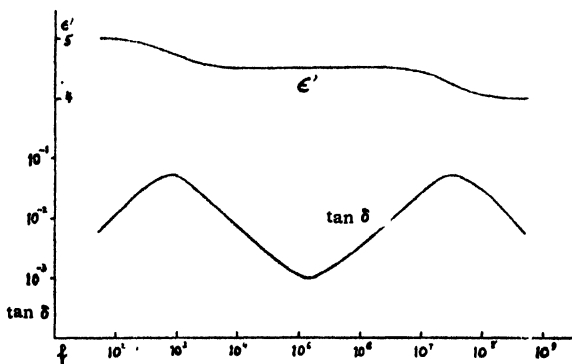


FIG. 4.—Dielectric constant and loss angle calculated ($\tau_0 = 10^{-4}$ sec.).

In order to show the two maxima more clearly, another calculation is given

in Fig. 4. ζ_0 is here 10^{-18} ($\eta_0 \sim 10^4$) and $\zeta = 10^{-22}$ ($\eta \sim 1$), $\tau_0 = 10^{-4}$ sec. The other data remain the same. We notice the two maxima, near $f = 10^3$ and 10^7 . This type of behaviour is characteristic of heavy oils, where peaks in $\tan \delta$ are found both at technical and radio frequencies.²²

(c) The peaks are often not so pronounced, but the whole range is

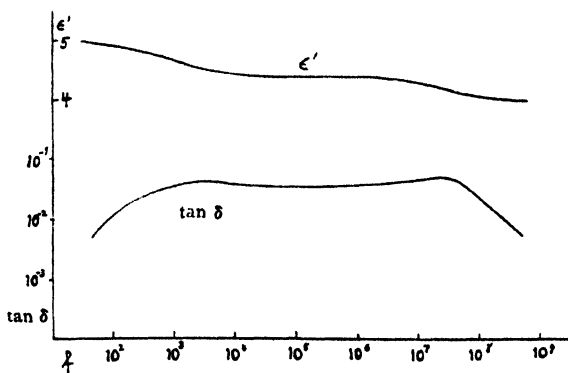


FIG. 5.—Dielectric constant and loss angle calculated ($\tau_0 = 10^{-4}$ sec., first power law).

rather smooth, $\tan \delta$ going through flat maxima and minima. It is possible that this behaviour can be reproduced by a circuit different from that in Fig. 1, as already mentioned. An assumption of equations for ζ' and γ' which follow a first power law with regard to $(\tau_0 \omega)$ would be more in keeping with

Philippoff's observations on structure-viscosity. Calculating the same case as before in Fig. 4, we obtain a flat curve for $\tan \delta$ (Fig. 5). Similar results have been obtained for instance by Strutt, for glass near 100°C .

Careful measurements on amorphous materials over the whole

²² A. Gemant, *Z. techn. Physik*, 1930, 11, 544.

frequency range were necessary in order to compare theory and experiment.

6. Ionic Mobility.

A great difficulty in checking any theory experimentally lies, as mentioned, in the fact of the overlapping of different mechanisms. In addition to the dipole losses, there are those according to the Maxwell-Wagner layer-theory, especially for low frequencies.

There is even another possibility. In applying the complex viscosity to the vibrational motion of singular ions in vitreous media, there appears for the ionic conductivity a value which must increase with increasing frequency. This provides another quite different explanation for the fact that the ohmic resistance of dielectrics for alternating voltage is generally much lower than that for continuous voltage. It seems as if the mobility had to increase also with increasing velocity. This would account to some extent for the usually observed increase of conductivity with field strength in dielectrics. The equations governing the motion of ions will be treated elsewhere.

Summary.

1. In order to explain the observed decrease with increasing frequency of the apparent viscosity in cases concerned with molecular vibrations in amorphous solids (acoustical waves, dielectric losses), the conception of a complex viscosity, V , is introduced instead of the simple real value (η). In other words: the Maxwellian theory which proved so useful for explaining the macroscopic behaviour of plastic bodies, is here applied to molecular vibrations. By this means account is taken both of the viscous and of the elastic displacements of the molecules. It is applicable to materials in any state of transition between liquid and crystal (generally referred to as the amorphous or vitreous state).

2. A special application of the theory to dielectric losses due to dipole rotation is given, and it is found that the results are qualitatively in accord with observations on glass, paraffin, etc. Losses are extended over a wide frequency range, and peaks may occur at two different characteristic frequencies, corresponding to the static viscosity and the damping of elastic vibrations. Often only the second one is detectable, yielding for this frequency range a much lower value of apparent viscosity than the static value.

The author is much indebted to Messrs. Metropolitan-Vickers Elec. Co. Ltd., Manchester, for a grant, enabling him to carry out this investigation.

REVIEWS OF BOOKS.

Neuere Massanalytische Methoden. By E. BRENNECKE, K. FAJANS, N. H. FURMAN and R. LANG. *Die Chemische Analyse*, edited by W. BÖTTGER, Band 33. (Stuttgart: F. Enke, 1935. Pp. xi + 211. Price (paper covers) 18 Marks.)

This volume of *Die chemische Analyse* contains sections on indicator corrections (Brennecke), ceric sulphate as oxidising reagent (Furman), iodate and bromate titrations (Lang), chromous sulphate as reducing reagent (Brennecke), oxidation-reduction indicators (Brennecke) and

adsorption indicators (Fajans). Each section gives an account of the theory, the details of the titration methods, the uses to which the method can be applied, and literature references. The newer methods of volumetric analysis have already found application in many directions in scientific and industrial laboratories, and the volume should be very useful in general in indicating the possible uses of such methods. It is authoritatively written and contains sufficient detail to make it really useful in the laboratory, the preparation of the reagents, for example, being given in full. The index covers, not only the reagents, but also the substances which can be determined, so that it is easy to find whether any particular titration is dealt with in the volume.

J. R. P.

X-Rays in Theory and Experiment. By ARTHUR H. COMPTON, Ph.D., Sc.D., LL.D., and SAMUEL K. ALLISON, Ph.D. (London: Macmillan & Co., Ltd., 1935. Price 31s. 6d. net.)

In the present state of knowledge of X-ray physics, it is no easy task to prepare a volume which has the quality entitling it to rank as a standard work upon the subject. The difficulties largely arise from the rapid progress of experimental physics throughout the world, and because new fundamental conceptions relating to a wide range of science have now been established by the mathematicians.

The results of observation, however, that fit in with theory and those independent theories that are subsequently found to be supported by experimental evidence, form an ever-widening circle of fact; it is one of the notable features of this book that the authors are able to present both aspects of the subject with a care and authority which gives their work precision and completeness. It is, perhaps, the most comprehensive attempt so far made to unite the two principal ways of regarding the nature of X-rays, *viz.* as electro-magnetic waves or as streams of particles. Mathematical analysis of the numerous problems attacked forms a large part of the volume, but it almost invariably relates to experimental work which is also described in detail.

It would serve no purpose to draw detailed attention to any particular section; each reader will, no doubt, seek out those portions which happen to interest him above all others. It is safe to say, however, that practically all known physical aspects of the subject seem to have been dealt with, and the authors have rendered a valuable service to physics in bringing together data and arguments which could otherwise only be found scattered throughout the scientific journals.

Some of us who remember the astonishment created by Professor Röntgen's announcement in 1885 had hoped to keep pace with the developments and literature relating to the new vista in science which seemed likely to be thereby opened up. Sir Oliver Lodge had expressed such a hope, but even he admitted a few years later that he felt overwhelmed by the vast mass of knowledge that was accumulating along many new directions as the outcome of Röntgen's discovery. At the present time, all that most of us can do is to know a small section of the subject; medical radiology alone, which is one of the most important applications, has already a vast literature of its own and is daily extending its practical usefulness.

The book under review, containing some 800 pages and numerous diagrams and other illustrations, as well as valuable appendices, and an author and subject index, has clearly been prepared with great care and vision. It is divided into nine main chapters, each having several subsections. The lay out and grouping of the subjects dealt with are excellent. Perhaps a better idea of the scope of the work can be given by quoting the headings of a few of these chapters. The first 52 pages are mainly introductory. Chapter II. (48 pages) deals with the "Production of X-rays." This chapter covers a wide range and includes references to "Energy and Intensity of Long-wave Trains," the effect of the thickness of the target on the characteristic radiation, the "Efficiency of X-ray Production," polarisation, quantum theories of the continuous spectrum, and so on. Both the third and sixth chapters are each divided into sections or parts, the former into four parts and the latter into two. Chapter III. deals exhaustively with the scattering of X-rays, and Chapter VI. with the intensity of reflection of X-rays from crystals.

There can be no doubt that this book, which is well printed and turned out, will fulfil a very real want. It has the merit of being written in a clear and interesting style, and can be unhesitatingly recommended to all who are making a serious study of modern X-ray physics.

C. E. S. P.

Acta Physicochemica U.S.S.R. Edited by A. BACH, A. BRODSKY, J. FRENKEL, A. FRUMKIN, I. GREBENSNIKOV, N. KURNAKOW, A. RABINOWITCH, A. RAKOVSKY, E. SCHPOLSKY, N. SEMENOFF, D. TALMUD, B. WYROPATJEFF. (Moscow: Onto-Editorial Office of Chemical Literature.)

The new physicochemical journal of the U.S.S.R. is now more than a year old. It has come into a stationary state by which one can estimate its future importance: it seems safe to say that it will become a permanent, and in many respects, a vital factor in scientific life. The present school of Russian physical chemistry is young; its first start was due to Frumkin who, in 1920, opened a new line for the investigation of the structure of double layers. This was followed a few years later by Semenov's discovery of the "cold explosions" of sulphur vapour with oxygen. These two sources can still be recognised in the now widely flowing current of physical chemistry in the U.S.S.R. Surface chemistry and gaseous kinetics, especially of chain reactions, are the dominant subjects; pupils and former collaborators of Frumkin and Semenov form a considerable part of the authors. An intermediate scene of action, in which both schools partake, has been found in heterogeneous catalysis, a subject favoured all over the globe by scientists anxious to prove their immediate utility to worldly authorities. The mathematical treatment of the mechanism of chemical reactions has also been started in the U.S.S.R. The theoretical group shows a singular ability to bring atomic dynamics into intimate relation with the field-work of chemistry.

One weakness can be felt; the lack of a strong school of organic chemistry in the U.S.S.R.; which is a necessary backing for the investigator in the fields now opening up before theoretical chemistry.

The *Acta Physicochemica* is tri-lingual: English, French and German. But although English is its editorial language, the majority of the contributions are at present written in German. Most of the papers appearing in the *Acta* would have previously been submitted to the *Zeitschrift für physikalische Chemie*. The U.S.S.R. scientists have sacrificed a great deal by giving all their papers to the new journal, which, for some time, will not provide them with such publicity as they previously enjoyed through publication abroad. The success which their efforts deserve will not be denied them; I feel sure that the new periodical will be indispensable in all laboratories of physical chemistry, and will take its place among the standard journals of our science.

Principles of Experimental and Theoretical Electrochemistry. By MALCOLM DOLE, PH.D. McGraw-Hill Publishing Co. Ltd. Pp. 549. Price 30s.

The author objects to the usual definition of electrochemistry as that part of chemistry mainly concerned with the interconversion of chemical and electrical energy, on the grounds that all chemical phenomena are now being interpreted on the basis of electrical interactions. For this reason a more restrictive view is adopted which lays stress on the experimental side of electrochemistry and regards the subject as consisting of the body of knowledge accumulated through the application of electric current or of electric or magnetic fields to the solution of chemical problems, and through the measurement of electric currents flowing in, or of potentials generated by, chemical cells. The contents of the book are determined by this definition, so that subjects usually included in electrochemistry, such as the theory and use of indicators, and solubility product, find no mention, and buffer solutions are dealt with in a page and a half. On the other hand, the inclusion of isolated chapters on "Dipole Moments" and on "Molecular Rays" is justified by the author's point of view. To follow to its logical consequences his definition of electrochemistry would, however, necessitate the consideration of such subjects as the study of the electron, the investigation of isotopes by the mass spectrograph and even some aspects of atomic disintegration. It is evidently unwise to attempt to define electrochemistry!

The method of treatment of the various topics in the book is essentially modern: in fact, objection may be raised that it is too modern. In connection with overvoltage, for example, the name of Caspari is not recorded, and the only theory which receives more than mention is one based on quantum mechanics. The Onsager and Debye-Hückel theories of strong electrolytes are discussed thoroughly, and the deduction of the equations of the latter authors is given in full, in spite of the somewhat difficult mathematics involved: this treatment has the advantage of emphasising the points at which approximations have been introduced. The testing of the Debye-Hückel equations by means of solubility measurements is described, but there is no mention of the application of the theory to osmotic data, to heats of dilution, or to partial molal volumes. Whenever thermodynamic treatment is required the methods of Willard Gibbs, involving chemical potentials, are used, leading to simple and rigid

deductions; these and the chapter on "Quantum Mechanics and Electrochemistry" will best be appreciated by readers who have mathematical inclinations. Interesting features of the book are the discussions of acids and bases, of liquid-junction potentials and of the glass electrode. In view of Dr. Dole's own important contributions to our knowledge of this electrode it is not surprising to find the subject treated at some length.

In considering the book as a whole, the reviewer feels that although it contains a wealth of interesting material it does not give a true survey of electrochemistry. In addition to the points already mentioned attention may be called to the following facts: in the description of conductivity measurement the theory of the A.C. bridge and of the valve oscillator is given quite fully, but the platinising of the electrodes is dismissed in one short sentence, and the general problem of solvent error is not considered. The glass electrode is treated at much greater length than is the hydrogen or the quinhydrone electrode, and not more than thirty pages are devoted to all aspects of irreversible electrode behaviour. The reader who appreciates these limitations will find much of value in Dr. Malcolm Dole's book; it is well illustrated and singularly free from typographical errors, so that the writer and publishers are to be congratulated on its production.

S. G.

Organic Solvents. Physical Constants and Methods of Purification.

By A. WEISSBERGER and E. PROSKAUER. Translated from the German Manuscript by R. G. A. New. (Oxford: The Clarendon Press. Pp. 212. 1935. Price 15s. net.)

This book, which is published for the first time and is not a translation of an existing work, consists of a series of tables giving the physical properties of a large number of organic solvents, and a second part dealing with methods of purification. It is intended for use in the laboratory, since the commercial aspects are not specifically dealt with, although the book cannot fail to be serviceable to technical users. Over 1400 references to literature are collected, and the compilation of data has obviously been very carefully carried through. The authors have accomplished a most useful piece of work which should lighten the task of many experimenters. The translation is very satisfactory and the printing and paper are very good. The very reasonable price at which the volume is published is commendable, and it deserves to be very widely used.

J. R. P.

ELECTRODEPOSITION OF ZINC AND CADMIUM ON ALUMINIUM AND ALUMINIUM ALLOYS.

BY B. K. BRAUND AND H. SUTTON.

Received 3rd December, 1934.

Introduction.

In view of the advances which have been made in recent years in the protection of aluminium and aluminium rich alloys by electrodeposits, and the possible utility of electrodeposits of zinc and cadmium particularly, experiments have been made to determine the protection afforded against corrosion under conditions simulating exposure to marine atmospheres and under actual conditions of marine exposure. Up to the time of commencing this work, the best deposits of zinc and cadmium on aluminium or aluminium rich alloy which had come to the notice of the authors had been applied to surfaces prepared for plating by light sandblasting. For many purposes, the slight roughening of surface and of thin electrodeposits subsequently applied is not objectionable. Tests have therefore been made to ascertain the merits of electrodeposits applied to sandblasted aluminium and aluminium alloy surfaces in comparison with other well-known methods of protection against corrosion.

While this work was proceeding, attention was paid to the use of other methods of preparing aluminium and aluminium-rich alloys for subsequent plating with zinc with a view to the production of adherent and smooth deposits. This work is described in Part II. of the present paper.

Experiments were also made to determine the current distribution between electrodes in a zinc sulphate plating bath, and in the same electrolyte in the throwing-power box. The results, given in the Appendix, illustrate the importance of "screening" in throwing-power work.

Part I. Investigation of Protection against Corrosion by Electrodeposits of Zinc and Cadmium.

Materials Used.—The materials plated were :—

Aluminium sheet	B.S.I. 2L16
Duralumin sheet	B.S.I. 2L3
Mild steel sheet	B.S.I. 2S3
Cast aluminium alloy	B.S.I. L5
Cast aluminium alloy	B.S.I. L11
Cast aluminium alloy (Y-alloy)	B.S.I. L24
Cast silicon-aluminium alloy	D.T.D.25

The test pieces cut from sheet material were 2 inches \times 4 inches and the cast alloy test pieces were cut from plates $\frac{1}{8}$ inch to $\frac{1}{16}$ inch thick, each

piece being 4 inches long. The plates were cast in sand moulds and the cast surfaces were not removed prior to preparation for plating.

Preparation for Plating.—All the samples were prepared for plating by sandblasting with fine sand and an air pressure not exceeding 10 lb. per sq. inch. This had been found to be satisfactory for aluminium and its alloys and no difficulty was experienced owing to grains of sand becoming embedded in the test piece so long as the air pressure did not exceed the given limit.

Plating Baths.—The zinc sulphate plating baths used were the four most suitable ones developed at Farnborough by Cocks.¹ They were all normal in respect of zinc sulphate and quarter normal in respect of sodium acetate.

Zinc sulphate ($\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$)	144 gms.
Sodium acetate ($\text{CH}_3\text{COONa} \cdot 3\text{H}_2\text{O}$)	34 gms.
Water to make up to	1 litre

The four sulphate baths differed only in the addition agents used in each, *viz.*,

- Bath (a) 1 gram per litre gum arabic.
- Bath (b) 25 grams per litre glucose.
- Bath (c) 0.1 gram per litre beta-naphthol.
- Bath (d) 0.1 gram per litre beta-naphthol + 0.25 gram per litre gum tragacanth.

The glucose used was described by the suppliers as "Glucose solid technical."

The zinc cyanide baths, also developed by Cocks, were as follow :—

	<i>Bath A.</i>	<i>Bath B.</i>
Zinc cyanide	59 gms.	56 gms.
Sodium cyanide	37 gms.	48 gms.
Sodium hydroxide	20 gms.	—
Ammonium hydroxide (0.88 S.G.)	—	29 c.c.
Water to	1 litre.	1 litre.

The cadmium plating bath was as follows :—

Potassium cadmium cyanide	62 gms.
Ammonium hydroxide (0.88 S.G.)	15 c.c.
Water to	1 litre.

Plating Conditions.—Sulphate baths were used with $p_{\text{H}4}$ and $p_{\text{H}5}$ and current densities of 10 amps. per sq. ft. and 30 amps. per sq. ft. The cathode was kept moving slowly during deposition.

Zinc cyanide baths were used with a cathode current density of 2 amps. per sq. ft. and 4 amps. per sq. ft., but mainly the latter value.

The cadmium cyanide bath was used with a cathode current density of 4 amps. per sq. ft. Three of the cadmium plated samples, A₁, A₂ and A₃, were given a thin undercoat of zinc by plating in the "B" zinc cyanide bath for 5 minutes at 4 amps. per sq. ft. The remaining samples were plated direct in the cadmium cyanide bath.

A thickness of 0.0005 inch was aimed at with all deposits. The current densities and corresponding periods of deposition are given below.

Sulphate baths	30 amps. per sq. ft.	14 mins.
	10 amps. per sq. ft.	40 mins.
Zinc Cyanide baths	4 amps. per sq. ft.	120 mins.
	2 amps. per sq. ft.	240 mins.
Cadmium Cyanide bath	4 amps. per sq. ft.	80 mins.

Most of the plating from the zinc cyanide baths was at 4 amps. per sq. ft. On mild steel the period of plating was 110 mins. and on L11 and L24 it

¹ H. C. Cocks, *Trans. Farad. Soc.*, 1930, 26, 517-26.

was 140 mins. These variations were due to the cathode current efficiencies on these materials differing appreciably from those on the other materials plated.

Corrosion Tests.

The corrosion test to which the samples were subjected was the intermittent sea-water spray test. The test pieces were suspended from thick glass rods by hooks made of thin glass rod. The tests were made in a shed, the south wall of which had been completely removed. This protected the samples from rain but allowed a free circulation of air. The test pieces were sprayed with a fine mist of sea-water three times a day during the period of test, which extended over two years.

Results of Corrosion Tests.

The corrosion-resistance of the samples was judged by appearance only. During exposure observations were made but care was taken in handling the samples not to dislodge corrosion product as it formed. At the end of the period of exposure the test pieces were examined, washed in cold tapwater and gently rubbed with the fingers, dried and again examined.

No mechanical tests were made on these samples to determine the loss of mechanical properties due to corrosion, but mechanical tests have been made on the samples in another series of tests, to which reference is made later.

Observations showed that the deposits obtained from the zinc sulphate plating baths were superior to those obtained from the zinc cyanide plating baths for protecting aluminium and its alloys. At first it was thought that the cadmium deposits were markedly inferior to the zinc cyanide deposits, but on account of previous experience of the deceptive appearance of corroded cadmium deposits, the samples were re-examined after dipping in 50 per cent. nitric acid. As a result of this test it was seen that the underlying aluminium and duralumin was not so seriously corroded as was thought at first, and it was considered that the cadmium deposits should be classified as equal to or slightly inferior to the cyanide zinc deposits.

Zinc Sulphate Bath.

The deposits from the sulphate baths at both current densities and both p_H values, all afforded good protection to aluminium and duralumin against corrosion.

The bath (a) containing gum arabic appeared to be distinctly better than the other sulphate baths for producing a protective deposit of zinc on aluminium and duralumin. This conclusion was true of the deposits formed at a current density of 10 amps. per sq. ft. or at 30 amps. per sq. ft. and also when the acidity of the bath was p_{H5} or p_{H4} . The most protective deposits were produced when the bath had a p_H value of 4.

The different zinc plating baths used appeared to give deposits, all of which afforded a similar degree of protection to mild steel sheet. Mild steel was not so well protected by zinc plating as was aluminium or duralumin sheet.

Deposits from the zinc sulphate-gum arabic bath gave satisfactory protection to the light casting alloys with the exception of Y alloy (L24) and in all cases the protection afforded was better than that of deposits produced in baths containing other addition agents. Although it was generally observed that zinc deposits produced on the casting alloys at 30 amps. per sq. ft. appeared immediately after plating to be superior to those obtained at 10 amps. per sq. ft. a corresponding superiority of protective action was not always observed.

The protective action of zinc deposited on the silicon-aluminium alloy from the sulphate baths was in all cases of a high order.

Zinc Cyanide Baths.

Deposits produced in bath B on aluminium afforded better protection than those produced in bath A. On duralumin, however, this order was reversed.

Cadmium Cyanide Bath.

It was observed that the protection afforded by the cadmium deposits was less satisfactory on aluminium sheet than on duralumin sheet. The thickness of the zinc undercoat had no obvious effect on the corrosion.

The moderate degree of protection of mild steel observed under the severe conditions of these tests should not be taken to indicate that the zinc deposits do not protect steel. For shorter periods or less severe conditions of exposure zinc plating forms a very satisfactory protection.

The present tests demonstrate that the electrodeposits of zinc and cadmium on aluminium alloys are at least as effective in protecting the underlying metal against corrosion as similar deposits upon iron and steel.

Protection against Loss of Mechanical Properties.

Observations and mechanical tests have been made on samples of aluminium and duralumin protected by electrodeposits of zinc and cadmium before and after 3 months' exposure to the atmosphere on a sea-beach above high tide mark. The main conclusions on that series of tests were that the mechanical properties of aluminium or duralumin sheet, plated in the sulphate or cyanide baths, were practically unaltered. The properties of a set of similar samples stored in the laboratory for a similar period were also unchanged.

The results of a series of comparative exposure tests of various coatings as protectives for duralumin gave some information on the relative protection provided by electrodeposits of zinc, high purity aluminium coatings (Alclad), anodic oxidation by the Bengough-Stuart process, and by various high class enamels and varnishes of types used in aircraft construction.

Sets of samples were exposed between tide-marks on the beach at Felixstowe and to the intermittent sea-water spray test at Farnborough for a period of two years. Samples H1 to H4 were plated at 4 amps. per sq. ft. in ammoniacal zinc cyanide solution, bath B of the present paper to which had been added 1 gm./litre of dextrin and samples H6 to H8 in the buffered solution of zinc sulphate containing 1 gram per litre of gum arabic, bath (a) of the series of sulphate baths mentioned in the present paper, after being prepared by sandblasting. The initial thickness of the deposits was about 0.0005 inch and after the corrosion tests it was found that the samples exposed to beach exposure tests between "wind and water" at Felixstowe had only about 0.00004 to 0.00005 inch or the equivalent amount of zinc coating left upon them in the case of the cyanide zinc deposits; a mere trace of zinc was still left on the samples which had received deposits from the sulphate bath, which alone showed intercrystalline corrosion after the test. Both the cyanide and sulphate deposits exposed to sea-water spray test at Farnborough showed very little loss of zinc, the deposits remaining after the tests being of the order of 0.0003 to 0.0004 inch thick. These observations show plainly that the immersion conditions encountered at regular intervals, and in agitated sea-water, had caused almost complete removal of the zinc deposits, but that there had been very little reduction in thickness of the zinc deposits exposed to the intermittent sea-water spray test. This result is not surprising, since in the first case there is an unlimited supply of fresh sea-water flowing over the surface during the periods of immersion while in the second case there is merely intermittent wetting of the samples by small fresh supplies of sea-water mist and virtually no washing of the samples. The average results of tensile tests on the samples are given in Table I.

TABLE I.—RESULTS OF MECHANICAL TESTS.

Material.	Duralumin.						"Alclad."		
Protective Coating.	Spar Varnish (Clear).			Aluminium-pigmented Spar Varnish.			Aluminium.		
Exposure Test.	None.	Felix-stowe.	S.W. Spray.	None.	Felix-stowe.	S.W. Spray.	None.	Felix-stowe.	S.W. Spray.
Mark.	—	A.	A1.	—	B.	B1.	—	C.	—
0.1 per cent. proof stress, $T/\text{in.}^2$	18.9	17.4	17.0	19.0	16.9	17.8	14.7	18.7	—
Maximum stress, $T/\text{in.}^2$	26.3	21.2	21.5	26.6	24.5	24.1	24.2	25.1	—
Elongation per cent.	17.5	3.5	4.8	18.5	8.8	7.5	18.0	15.9	—

TABLE I. (Contd.).

Material.	Duralumin.												
Protective Coating.	None.	D.T.D. 63 Enamel (Cellulose).		D.T.D. 62 Varnish (Oil Base).		Anodised.				Zinc Plated.			
						Lanolined.		Greased.**		Cyanide Bath.		Sulphate Bath.	
Exposure Test.	None.	Felix-stowe.	S.W. Spray.	Felix-stowe.	S.W. Spray.	Felix-stowe.	S.W. Spray.	Felix-stowe.	S.W. Spray.	Felix-stowe.	S.W. Spray.	Felix-stowe.	S.W. Spray.
Mark.	—	D1.	D2.	E2.	E1.	F1.	F2.	G2.	G1.	H2.	H4.	H7.	H8.
0.1 per cent. proof stress, $T/\text{in.}^2$	19.3	18.5	18.7	16.3	17.8	17.9	18.8	18.7	19.0	17.0	18.5	17.0	18.2
Maximum stress, $T/\text{in.}^2$	27.0	21.3	25.1	18.9	22.4	23.6	24.1	25.2	26.6	24.4	27.1	24.3	27.1
Elongation per cent.	17.5	6.9	11.3	1.7	5.5	7.2	7.0*	12.8	15.7	7.0	11.9*	6.7	12.7

* One of the three test pieces failed near the head, and the elongation value was probably reduced appreciably in consequence.

** With a proprietary lanolin preparation.

These results indicate that the protection afforded, under the conditions of the tests, by the zinc electrodeposits is inferior to that afforded by the high-purity aluminium coating on "Alclad" sheet, but is of the same order as that afforded by anodic treatment by the Bengough-Stuart process supplemented by application of grease. They further show the protection to be superior to that provided by the application of the various varnishes and enamels employed in the tests. The tests showed practically no difference between the cyanide and sulphate deposits from the point of view of protective influence.

Part II. The Preparation of the Surface of Aluminium and its Alloys for Plating with Zinc.

Preliminary Discussion.

In view of the useful degree of protection of aluminium and aluminium alloys by zinc electrodeposits observed in our corrosion tests of samples, it was desired to develop methods of preparing these materials for the reception of zinc electrodeposits.

In previous work² good, adherent deposits have been obtained on sandblasted surfaces. Sandblasting is somewhat objectionable for the following reasons :

1. The roughness of the surface persists through the deposits.
2. Thin sheet material is liable to buckle.
3. The treatment of large surfaces is expensive.
4. Sandblasting is liable to be dangerous to the health of operators.

In view of these objections, a search has been made to find a means of preparing aluminium and its alloys for plating without unduly roughening the surface of the material.

When commercial aluminium or aluminium-rich alloy is pickled in caustic soda, aluminium is dissolved with evolution of hydrogen and other elements present remain as a slime on the surface of the material. This slime is not readily detached, and its removal is one of the problems which has to be overcome in order subsequently to obtain satisfactory electrodeposits on the pickled surface.

Methods Developed by Other Workers.

Work³ used hydrochloric or hydrofluoric acid, which roughened the surface of the aluminium or alloy and secured adhesion by keying the deposit to the prepared surface. For nickel plating he recommended an acid dip containing a nickel, iron or manganese salt, the appropriate metal being deposited on the aluminium by chemical replacement and forming a satisfactory preparation for the deposition of nickel.

Work also mentioned briefly a method of plating on smooth surfaces which consisted of plating from a zinc cyanide bath of the following composition as the first stage :

Zinc oxide	30	gms. per litre.
Sodium cyanide	30	" "
Ammonium hydroxide (0.90 S.G.)	33	" "
Gelatin	5	" "

The bath was used cold at a current density of 4.5 amps. per sq. ft. He stated that a 5 minutes' plate gave a satisfactory undercoat for other metals but good protection against corrosion was obtained only if zinc alone were deposited ; subsequent heat-treatment was beneficial. No details of the preparation for plating in this bath were given.

In a later article,⁴ Work described a method of preparing aluminium alloy die castings for nickel plating. For this purpose he used a nitric-hydrofluoric acid dip which dissolved the eutectic but allowed the solid

² H. Sutton and A. J. Sidery, *J. Inst. Met.*, 1927, 38, 241-57.

³ H. K. Work, *Metal Industry (London)*, 27, 7, 1928, 81 *et seq.*

⁴ H. K. Work, *Metal Progress*, April, 1931.

solution to remain unattacked. This method roughened the surface and produced keying.

In the authors' experiments, methods of cleaning which involved a hydrochloric acid dip followed by plating in Work's zinc bath gave deposits which were slightly less rough than those on sandblasted surfaces. A bath was made up to Work's formula but the gelatin was omitted on account of the marked similarity of this bath to that developed by Cocks * which was known to be capable of giving satisfactory deposits without colloidal additions.

Tests were made on small pieces of duralumin sheet which received the following treatments in sequence :—

1. Cleaned with benzol.
2. Pickled in 10 per cent. caustic soda for 10 minutes.
3. Dipped in 50 per cent. hydrochloric acid for 30 seconds.
4. Rinsed and scrubbed.
5. Plated in cyanide bath at 4 amps./sq. ft. for varying periods.
6. Plated in sulphate bath * at 15 amps./sq. ft. for 25 minutes.

All of the baths were kept within the range $20^{\circ}\text{C.} \pm 3^{\circ}\text{C.}$ The necessary washings were given between each operation. Samples plated in the cyanide bath for periods up to 15 minutes had smooth deposits and excellent adhesion although some slight blistering occurred at the edges. Prolonging the period of deposition caused more extensive blistering and less satisfactory adhesion. Addition of gelatin to the cyanide bath caused marked gassing at the cathode and dark coloured fine grained deposits were obtained. The final sulphate deposits blistered and adhesion was less satisfactory than when no gelatin was added.

A method of preparation, also for subsequent plating with nickel, devised by Ballay * consisted of immersing the aluminium or alloy, after suitable preparation, in a hot ferric chloride bath containing free hydrochloric acid. The concentration of iron varied from 6 to 22 gms. per litre and the free hydrochloric acid from 0.1 N to 0.7 N according to the material to be treated.

A small bath was prepared which contained 15 gms. per litre of iron and was 0.5 N with respect to hydrochloric acid. Samples of aluminium and duralumin sheet were prepared by cleaning with benzol followed by scouring with Sheffield lime and washing. After receiving this treatment the sheets were dipped in Ballay's solution for periods up to one minute, washed and plated in the zinc sulphate bath. Adherent zinc deposits free from blisters were obtained on aluminium. On duralumin small blisters formed but did not affect the general adhesion.

After immersion in the ferric chloride bath an adherent dark grey deposit was observed to have formed on the duralumin or aluminium. Various tests indicated that a thin film of iron had been deposited which was not readily detached by mechanical means. Drying of the treated pieces during transfer to the plating bath from the hot dipping bath appeared to result in entirely unsatisfactory deposits.

Some work was done on this process before the German paper by Ballay * was received. In this second paper by Ballay mention was made of an electrolytic cleaning process in 10 per cent. sodium carbonate solution but no details were given. When this method was tried in our laboratory and the work was treated anodically, the surface became pitted and gelatinous precipitates were formed. Cathodic treatment was fairly satisfactory with aluminium but was ineffective with duralumin.

* H. C. Cocks, *J. Electroplaters' and Dep. Tech. Soc.*, Vol. 5, 1929-30, p. 83.

* As used by Cocks, $1\text{ N ZnSO}_4 \cdot 7\text{H}_2\text{O}$, $\text{N}/4$ Sod. Acetate, 1 g/l gum arabic pH 4.0, C.D. 15 amps./sq. ft.

* M. Ballay, *Comptes Rendus*, 1930, 305-8; *Die electrolytischen Niederschläge auf Aluminium . . .*; *Mitt. des Nickel Informationsbüro*, Frankfurt a.M.

Substitution of zinc for iron in the Ballay process was attempted. *This reduced the ebullition on immersion in the hot bath and a deposit of metallic zinc could not be detected. Satisfactory preparation for plating was not obtained.*

Preparation in Ammonia Solutions.

As aluminium does not act as a true anode in most electrolytes the choice of solutions in which to clean the surface was limited. A wide range of electrolytic and simple immersion treatments in different solutions was employed in exploratory work, and most of the treatments resulted in the production of blistered deposits when the samples were subsequently plated with zinc.

Anodic cleaning in 10 per cent. ammonia gave promise of being an effective method and some satisfactory electro-deposits were obtained on samples prepared in this way. A pale straw-coloured film was frequently produced by this ammonia cleaning and in some cases this was observed to have become detached during plating. If caustic soda-pickled duralumin was allowed to remain in running tap-water the black slimes gradually turned a pale straw colour, resembling closely the behaviour of duralumin when anodically treated in ammonia. It appears that in both cases oxidation played an important part. Further, pickled duralumin when given a prolonged washing in running water required less time for anodic cleaning than material which was given a short washing only.

These experiments led to an attempt to plate direct upon material prepared by the Bengough anodic oxidation process,⁷ but the deposits were unsatisfactory.

Anodic cleaning of duralumin samples in ammonia on a 12-volt circuit indicated that a good preparation could be obtained in 2 hours, but shorter treatments would be unreliable. The addition of small amounts of copper to the ammonia increased the tendency to produce blistered deposits and did not improve adhesion. The adhesion on polished duralumin was of a low order. Anodic cleaning in a 10 per cent. ammonium chromate solution produced a very white surface and polarisation was less marked than with ammonia. Zinc deposits on material prepared in this way had a good appearance but did not adhere well.

It was found that under the simple conditions of the experiments here recorded, good results could not always be obtained. During anodic treatment it was observed that cleaning started at the bottom corners of the sheet and spread along the edges and then towards the centre or top. Further zones followed the formation of the cleaned surface and their behaviour varied during plating, the outer edge usually suffering from poor adhesion and blistering. If the voltage applied was low or the ammonia solution fresh or of high concentration the position of the zones was generally reversed.

Experiments showed that after a used ammonia bath had stood for a day or more a skin of aluminium hydroxide formed on the surface, and that used baths required a lower voltage for satisfactory cleaning than fresh ones. With a much used ammonia bath pinholes in the zinc deposit appeared and later the formation of network deposits was observed. This was thought to be due to saturation with alumina or to the increase in the carbonate content of the bath.

Though the experiments on anodic pickling of aluminium in ammonia solutions indicated that aluminium and surface films of oxide dissolve under this treatment, the aluminium apparently behaving as an anode to some extent, the results obtained were not sufficiently reliable to suggest that the method would be one suitable for practical application.

⁷ *Anodic Oxidation of Aluminium and its Alloys*, H.M. Stationery Office, 1926; also G. D. Bengough and H. Sutton, *Engineering*, 1926, 122, 274-7.

Preparation in Sodium Zincate.

Preparation of aluminium and duralumin surfaces for plating by anodic treatment in caustic soda solutions containing sodium carbonate was tried without marked success. It was decided to ascertain whether sodium zincate would replace the sodium carbonate addition with the possible deposition of a small amount of zinc, or, if zinc hydroxide formed part of the film produced, whether it might be readily dissolved in the plating bath leaving the aluminium surface clean to receive the electro-deposited zinc.

To an approximately 0.2 *N* solution of caustic soda a small addition (approximately 0.25 per cent.) of zinc oxide was made. This did not appear to dissolve to any appreciable extent, but it was found that on immersing a piece of aluminium in the solution a deposit of zinc was formed on the surface. Several attempts were made to use this bath for anodic cleaning but without any great success.

It was noticed that in some cases the immersion-deposit of zinc formed on the surface of the aluminium was very adherent; aluminium and duralumin samples were therefore cleaned in caustic soda, scrubbed with Sheffield lime, dipped in the sodium zincate bath and after washing were plated in the zinc sulphate bath. Some satisfactory deposits with very good adhesion were obtained in this way, and it was decided to investigate the possibility of using this method of preparation in preference to anodic cleaning in ammonia or caustic soda solutions.

Cast electrolytic zinc was allowed to dissolve in a 7 per cent. caustic soda solution until a concentration of approximately one gram per litre of metallic zinc was obtained. A piece of mild steel sheet placed in the bath in metallic contact with the zinc hastened the solution which was otherwise very slow, even when the bath was heated to incipient boiling. After 24 hours the rate of solution of zinc had become very slow and it appeared that some degree of equilibrium between the zinc and the electrolyte had been attained. No precipitate of zinc hydroxide was observed.

The use of this bath as a preparation was tried on various alloys as well as on commercial aluminium sheet. The samples were of small size—up to 2 inches \times 4 inches—and were first degreased with benzol when necessary, then pickled in 10 per cent. caustic soda solution, washed and whitened in 10 per cent. nitric acid, washed and dipped in the zincate bath for 15 to 30 seconds, washed and plated in the zinc sulphate bath at 15 amps./sq. ft. current density for 30 minutes.

Casting alloys L24 (Y-alloy), L11, L5 and silicon-aluminium alloy D.T.D.25 of the nominal composition stated below were treated in this way

	Copper. Per Cent.	Nickel. Per Cent.	Magnesium. Per Cent.	Zinc. Per Cent.	Silicon. Per Cent.
L24	4	2	1.5	—	—
L11	7	—	—	—	—
L5	12.5	—	—	3.0	—
D.T.D.25 . .	—	—	—	—	1.2

and excellent deposits were obtained on them without difficulty. All these alloys, except the D.T.D.25, were etched by the caustic soda and a marked macro-structure consisting of equiaxed grains was rendered visible, particularly in the case of the Y-alloy. This macro-structure was still clearly visible after plating with a deposit of zinc 0.0005 inch thick.

The alloy samples were sand cast plates approximately 0.25 inch thick and had machined edges. Roughnesses in the surface were well covered with zinc, but it should be noted that actual cavities in the casting did not appear to outcrop on the surface. In some later work on castings with machined parts which had cavities outcropping on the surface some difficulty was experienced in obtaining a deposit up to the edges of the cavities,

but where the roughness of the surface did not include very sharp changes in direction of the surface no difficulty was experienced in covering the whole sample satisfactorily. "As cast" surfaces generally appear to be free from outcropping cavities of the type which renders even deposition difficult except possibly when loose grains of sand are embedded in the metal and are later removed.

Small samples of aluminium and duralumin sheet were similarly prepared and plated, good deposits being obtained. Adhesion was good and the deposits were free from blisters. Composite specimens were then prepared by joining pieces of aluminium and duralumin sheet by a roll joint and after preparation, plating with 0.0005 inch of zinc. There seemed to be little difficulty in obtaining a satisfactory deposit on the duralumin part but it was only after several attempts that a satisfactory deposit was obtained on the aluminium sheet.

After this, further attention was paid to the preparation of aluminium sheet alone, and it was found that the method of preparation was unreliable. If the aluminium was prepared for the first time, on dipping in the zincate bath a dark coloured deposit of zinc was formed which was non-adherent and generally of an unsatisfactory nature. It was found, however, that if this deposit was dissolved off in the nitric acid dip or even if it was brushed off under water and the aluminium was again dipped in the zincate bath, a more satisfactory preparation was obtained.

This method of preparation has been used for subsequent deposition of nickel and chromium by Altmannsberger⁸ who states that if the deposit of zinc is grey, he dips it in nitro-sulphuric acid mixture and again dips it in the zincate bath and obtains a silvery white deposit of zinc. It should be mentioned that Altmannsberger was depositing on articles of aluminium and its alloys that had been buffed prior to plating.

In an attempt to overcome the difficulty of the unsatisfactory first deposit on some of our samples, higher temperatures for the zincate bath were used. At 50° C. a satisfactory flash of zinc was obtained on aluminium at the first attempt, but if the period of dipping was longer than a few seconds, there was an obvious hydrogen evolution and the deposit darkened and eventually tended to strip off the aluminium sheet. Further tests indicated that satisfactory deposits of zinc could be obtained with the zincate bath at 90° C., but the period of dipping had to be of very short duration.

Satisfactory deposits produced up to this stage withstood bending, in the case of duralumin up to fracture and in the case of aluminium sheets when subjected to a close bend and then re-opened. When aluminium sheet was very severely bent the zinc deposit was observed to crack along the bend but did not become detached even if the samples had originally been buffed.

With the best samples, neither heating on the hot plate for 20 minutes at a temperature below the melting point of zinc, nor heating an edge of the sheet in a blowpipe flame produced any blisters or detached the zinc deposit.

During the work it was found that the presence of a small amount of lead in the nitric acid dip invariably produced blistered and poorly adherent deposits.

The foregoing experiments indicated the possibility of suitably preparing aluminium and duralumin and certain casting alloys for plating in the zinc sulphate bath. It was thought that the use of nitric acid, and in particular strong acids like the Smith and Velarde⁹ mixture would be unobjectionable for the preparation of small articles, but expensive and difficult for use on large pieces of work, for example, large sheets of duralumin.

During some previous work it had been observed that anodic treatment

⁸ K. Altmannsberger, *Chemiker Z.*, 1931, **55**, 709

⁹ Smith and Velarde, *Metal Industry (London)*, 1931, 297.

in dilute sulphuric acid removed the slimes remaining after pickling in caustic soda, so it was decided to investigate this method.

A cell was made up containing 5 per cent. by volume of sulphuric acid in distilled water and two lead cathodes. The pieces of material being cleaned were suspended midway between the cathodes. The voltage between the anode and cathodes was carefully controlled and for the first experiment on duralumin was kept at 2 volts for 5 minutes, the specimen washed, zincate dipped, anodically treated again at 2 volts for 1 minute, zincate dipped and plated in the sulphate bath. The deposit was smooth but matte, adherent, and did not blister even after 30 minutes on the hot plate.

A small piece of a cast duralumin billet was anodically cleaned at 1.6 volts and dipped once only in the zincate bath. The deposit was again satisfactory.

A piece of aluminium sheet was prepared by anodic cleaning for 30 seconds at 6 to 10 volts, and zincate dipping for 2 minutes when the deposit was observed to darken slightly. After plating, the deposit was adherent and 10 minutes on the hot plate only caused a few very small blisters to form near one of the points of suspension for plating. A piece of duralumin prepared and plated in the same way had a good deposit free from blisters. It was of interest to note that although the macro-structure of the duralumin was clearly visible after anodic cleaning, the deposit was matte and no trace of the duralumin macro-structure could be seen after plating.

Further work showed that some part of the process was not under satisfactory control and several samples which were plated became blistered or the deposit was not properly adherent. Various expedients were tried in an attempt to overcome the difficulty. It was thought that a trace of tin might have been present in the zincate bath as an impurity and have assisted in making a good preparation of the surface. Additions of sodium stannate were found to render the bath more stable and aluminium or duralumin sheets could be immersed for much longer periods (certainly up to 10 minutes) without the production of a dark coloured deposit or the obvious evolution of hydrogen. Good preparation was obtained with aluminium, duralumin and casting alloys. It was also found that satisfactory zinc deposits could be obtained on aluminium and duralumin sheet in the ammoniacal zinc cyanide plating bath although in this bath there appeared to be a greater tendency to blister than in the acid sulphate bath.

It was observed that material prepared for plating by the zincate process could be plated in the sulphate plating bath at a lower p_H value than material prepared by sandblasting. This appears to be due to the roughness of a sandblasted surface favouring the deposition of hydrogen. Duralumin prepared by the zincate process was successfully plated at a p_H of 3.6 measured by a capillator using bromo-cresol green or bromo-phenol blue as indicator. Attempts to electrodeposit zinc on aluminium from the zincate bath were unsuccessful.

A zinc chloride bath of the following composition ¹⁰ was found to give satisfactory deposits on material prepared by the zincate method.

Zinc chloride	136 gms. per litre.
Aluminium chloride	20 " "
Sodium chloride	243 " "

This bath was worked under similar conditions to those used with the sulphate bath, p_H 4.0 and current density of 15 amps./sq. ft. and good, fine grained deposits were obtained on material prepared by the zincate process. The deposits were slightly darker than those obtained in the sulphate bath but lighter than cyanide zinc deposits. Gas pitting was of rarer occurrence than in the sulphate bath.

¹⁰ M. R. Thompson, *J. Am. Electroch. Soc.*, 1926, **50**, 215.

Summary of Results.

None of the methods developed by other workers was found to be entirely satisfactory. The method evolved by Work had the advantage that no metal other than zinc need be deposited. Unfortunately his method did not form a satisfactory preparation for deposition from the zinc sulphate bath. Deposits made in sulphate baths on material prepared by plating in Work's bath were prone to blister.

The method due to Ballay could probably be made to produce a satisfactory preparation but would require very careful control of the ferric chloride bath. This method is probably satisfactory for small articles, but for larger articles the difficulty of preventing drying of the work before it can be placed in the washing tank would cause trouble.

Numerous tests were made on methods of electrolytic cleaning and the method in this group found to give the most promising results was anodic cleaning in ammonia solutions, but in general electrodeposits subsequently applied were satisfactory only on parts of the prepared article.

Solutions of sodium zincate have been found to react with aluminium and aluminium-rich alloys, some solution of aluminium and deposition of zinc resulting. Under favourable conditions the zinc deposit is adherent and forms an excellent undercoating for the further deposition of zinc from the zinc sulphate plating bath.

The zincate bath was, however, rather liable to give dark coloured and non-coherent deposits. Frequently, if such a deposit was dissolved off and the aluminium again dipped, a satisfactory deposit was obtained. The addition of a small proportion of sodium stannate to the zincate bath was found to cause the deposits to be more reliable and no evolution of hydrogen occurred.

The experiments showed that aluminium-rich casting alloys can be prepared and plated by this process very satisfactorily. Aluminium and duralumin sheet was satisfactorily prepared and plated, but greater care was required than with the casting alloys.

It was found that zinc could be deposited from sulphate baths of lower p_H value when the article to be plated had been prepared in the zincate bath than when it had been prepared by sandblasting. This was attributed to the absence of roughening produced by sandblasting.

Deposits were satisfactorily produced on aluminium and its alloys prepared by the zincate method, in a zinc chloride plating bath.

APPENDIX.

Note on Current Distribution in a Zinc Sulphate Plating Bath.

In a previous paper ¹¹ by one of us, determinations of throwing power of various zinc plating baths by the Haring and Blum method ¹² were described. In view of the general plea for a simpler and more practical method of determining throwing power, and the various forms of cell which have been proposed for use in this connection, *e.g.*, that described by Field,¹³ it was considered to be of interest to determine the current distribution between electrodes in different positions. This was done with the orthodox and other arrangements of electrodes in the throwing-power box, and with similar electrodes suspended in a large plating bath.

Experimental Work.

For these experiments, the normal zinc sulphate plating bath was used, being considered suitable owing to its low throwing power. Throwing power tests and

¹¹ B. K. Braund, *Trans. Farad. Soc.*, 1931, **27**, 661-74.

¹² Haring and Blum, *Trans. Am. Electroch. Soc.*, 1923, **44**, 313.

¹³ S. Field, *Proc. Electrodep. Tech. Soc.*, 1932, 83-90.

the smallness of variation of cathode current efficiency with cathode current density¹¹ indicated that the difference between the primary and secondary current ratios was small, and that therefore secondary current ratio determinations would give an indication of the primary current ratios.

To determine the current distribution when the two half cathodes were on the same side of the anode in the throwing-power box, the apparatus had to be modified. The Haring-Blum box and perforated anode were used, but the half cathodes were of half the width and were secured to grooves on opposite sides of the box by spring clips. Care was taken to maintain the half cathodes in their correct positions and their backs and cut edges were "stopped off" with paraffin wax. The cathodes were made of duralumin sheet, and were sand-blasted on the unstopped surface.

Electrical connections are given in Fig. 1. "V" was a millivoltmeter, A_2 and A_3 ammeters used to measure the current flow to each half cathode and R_1 a rheostat of approximately 3 ohms resistance capable of fine adjustment. R_2 was a rheostat for adjustment of the total current flow which was measured by ammeter A_1 .

The reason for the inclusion of millivoltmeter "V" and rheostat " R_1 " in the circuit was to make possible the adjustment of the current distribution to the two half cathodes so that

there was zero potential difference between the two half cathodes. This was rendered necessary by the inclusion of the two ammeters " A_2 " and " A_3 " in the circuit. When making a throwing-power determination the two half cathodes were connected by a heavy copper conductor of low resistance, thus reducing any P.D. between the two half cathodes to a negligibly low value. The inclusion of two ammeters and several metal to metal junctions between the two half cathodes increased the resistance, and it became necessary to provide means of adjusting the potential difference of the two half cathodes to zero. When this adjustment was made the two half cathodes virtually became, from an electrical point of view, a single cathode.

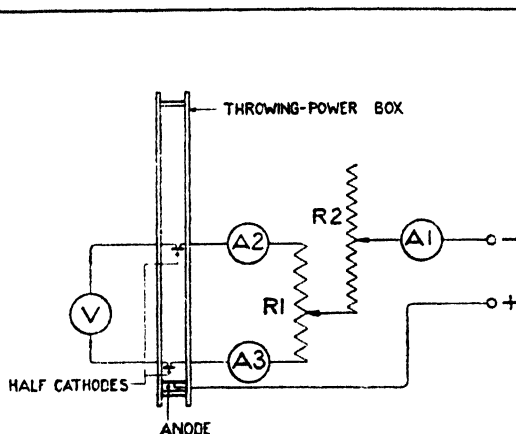


FIG. I THROWING POWER BOX EXPERIMENTS

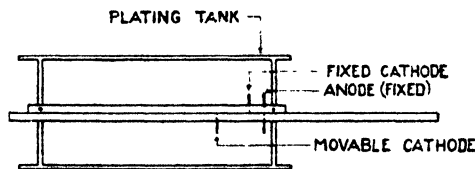


FIG. II PLATING BATH EXPERIMENTS

A mean current density of 18 amps per sq. ft. was maintained. During some preliminary experiments there was some difficulty in keeping the two half cathodes at the same potential. This was found to be due to the growth of trees on the edge of the half cathode nearest to the anode. These were detached by means of a clean piece of wood and by frequent removal were prevented from again growing to appreciable size.

The half cathode nearer to the anode was kept 5 cms. away from the anode throughout the experiments, and the more remote half cathode was moved 5 cms. further away between readings. It should be noted that each half cathode and the anode extended from above the level of the electrolyte to the bottom of the box and that one edge was fixed in a groove in the side of the box. After a preliminary experiment, the "stopping off" of the edges of the half cathodes was improved and the difficulty due to treeing was minimised.

Throughout these experiments the temperature of the bath was within the range $20^{\circ}\text{C.} \pm 2^{\circ}\text{C.}$

The results of the first series of readings are recorded in Table II. The first column, "Distance Ratio," gives the ratio of the distances of the half cathodes from the anodes and in the calculation of "improvement per cent." the Distance Ratio was regarded as the primary current ratio as in Haring and Blum's notation.¹ The next two columns may be regarded as the I_n and I_r and the fourth column, "Secondary Current Ratio," was calculated from observations of current corresponding with the various distance ratios. The last column, "Improvement Per Cent.," would be "Throwing Power" if the box were used in the orthodox manner.

TABLE II.

Distance Ratio (D.R.)	Current to near Half Cathode. Amps	Current to remote Half Cathode. Amps	Secondary Current Ratio (S.C.R.)	$\frac{S.C.R.}{D.R.}$	Improvement Per Cent $\frac{D.R. - S.C.R.}{D.R.} \times 100.$
First Series.					
2 : 1	1.595	0.410	3.89	1.95	-95
3 : 1	1.715	0.275	6.25	2.07	-108
4 : 1	1.779	0.210	8.40	2.1	-110
5 : 1	1.790	0.174	10.0	2.0	-100
6 : 1	1.820	0.149	12.0	2.15	-115
7 : 1	1.825	0.130	14.0	2.0	-100
8 : 1	1.836	0.113	16.2	2.03	-102
9 : 1	1.870	0.094	19.9	2.21	-121
10 : 1	1.875	0.091	20.6	2.06	-106
Second Series.					
2 : 1	1.230	0.740	1.66	0.83	17.0
3 : 1	1.320	0.625	2.12	0.71	20.3
4 : 1	1.395	0.503	2.78	0.69	30.5
5 : 1	1.450	0.490	2.96	0.59	40.1
6 : 1	1.500	0.442	3.40	0.57	46.7
7 : 1	1.535	0.401	3.84	0.55	45.1
8 : 1	1.565	0.380	4.12	0.52	48.5
9 : 1	1.595	0.340	5.25	0.58	41.7
10 : 1	1.650	0.320	5.17	0.52	48.3
Third Series.					
1 : 1	0.990	0.990	1	—	—
2 : 1	1.145	0.784	1.46	0.73	27.0
3 : 1	1.250	0.690	1.81	0.60	39.7
4 : 1	1.320	0.620	2.13	0.53	46.8
5 : 1	1.370	0.565	2.41	0.48	51.8
6 : 1	1.420	0.518	2.74	0.46	54.3
7 : 1	1.450	0.477	3.04	0.43	56.6
8 : 1	1.490	0.440	3.39	0.42	57.6
9 : 1	1.510	0.412	3.67	0.41	59.2

Improvement Per Cent. as used here is the Distance Ratio minus the Secondary Current Ratio divided by the Distance Ratio, all multiplied by one hundred,

$$\text{or} \quad \frac{D.R. - S.C.R.}{D.R.} \times 100 \text{ per cent.}$$

It should be noted that this value differs from the Throwing Power in that under the conditions of experiment the distance ratios do not equal the primary current ratios, owing to the introduction of another factor not affecting the bath used by Haring and Blum, *viz.*, screening of the distant half cathode by the nearer one.

The readings recorded in Table II. were taken 1 minute after completing the electric circuit in each case. This was done owing to the difficulty of making all necessary adjustments with certainty in a shorter time. It was found that taking the readings as soon as the resistances were adjusted increased the irregularities in the readings.

In the next experiment ("Second Series") a similar set of readings was taken with the electrodes suspended in a relatively large plating bath, so as to avoid such excessive screening by the sides and bottom of the bath.

The containing vessel of waxed wood was rectangular in plan, 27.5 cms. \times 59.8 cms. and filled with the solution to a depth of 17.5 cms. The zinc anode was 10.4 cms. wide, and the half cathodes 5.2 cms. wide, and all were immersed to a depth of 10 cms. The anode and one half cathode were mounted 5 cms. apart on a batten which spanned the vessel lengthways, so that the anode was close and parallel to one end of the vessel and equidistant from the sides. The fixed half cathode covered one half of the anode when regarded in end elevation. The movable half cathode was on a similar batten and in end elevation covered the remaining half of the anode. The batten carrying the anode was secured to the vessel, and the other batten carrying the movable half cathode could be moved parallel to the fixed batten so as to give the required distance ratios. A plan of the arrangement is given in Fig. 2.

The electrical connections and manipulation were the same as in the previous experiment. As before, the back and edges of the half cathodes were stopped off with paraffin wax.

A further experiment was made with the two half cathodes on opposite sides of the anode in the large plating bath, in the same relative positions as in the throwing-power box. The same half cathodes were used, and these as well as the anode cut down to half its original width, were supported by the same battens. The movable half cathode was supported on an offset bracket so that it was in line with the other two electrodes.

For comparison with these values, the throwing-power values, obtained with the same arrangement of electrodes in the throwing-power box, *i.e.*, with extreme

TABLE III

Primary Current Ratio.	Corrected Primary Current Ratio.	Corrected Throwing Power Per Cent.
2 : 1	2.093 : 1	+ 1.10
3 : 1	3.167 : 1	+ 1.17
4 : 1	4.260 : 1	+ 0.92
6 : 1	6.353 : 1	- 0.95
9 : 1	9.393 : 1	- 3.65

The corrections made in the second and third columns were to overcome the error due to alteration of the conductivity of the electrolyte caused by uneven heating on opposite sides of the anode.

The cathode material in all these experiments was sandblasted duralumin sheet. All current readings were, however,

taken when zinc was already deposited on the sandblasted surface.

The "improvement per cent." values in the four tables are plotted against distance ratios in Fig. 3. It will be noticed that the points from Table IV. lie on a regular curve, and that those on curves 1 and 2 are more irregular. It is thought that this may be due to the formation of trees, and to the relatively sharp edges of the half cathode nearer to the anode forming more effective screening than a smooth edge of greater radius, thus virtually enlarging the electrode area. The irregular formation of trees would account for the irregularity of some of the points. When the half cathodes are on opposite sides of the anode this screening effect does not arise.

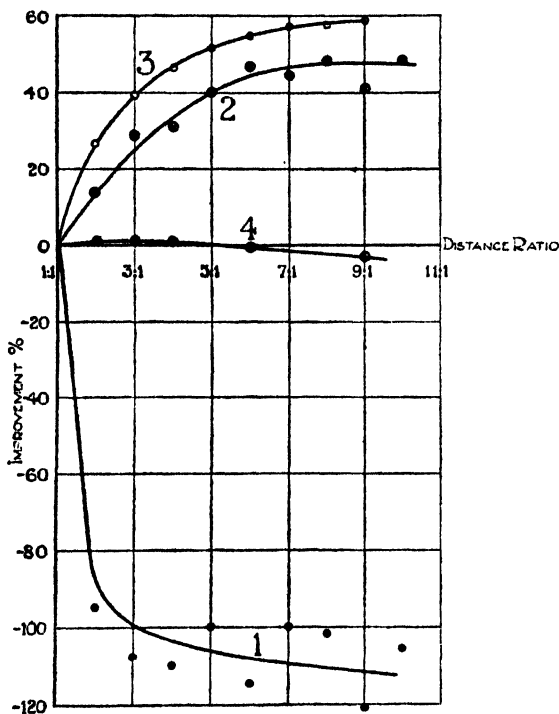
Discussion of Results.

The experiments here recorded give values of secondary current distribution in a plating bath known to have a throwing power very nearly equal to zero. The observed values of secondary current ratio may therefore be taken as approximating closely to primary current ratios.

When the half cathodes were on the opposite sides of the anode, the values of the "improvement per cent." of the current distribution ratios

FIG. III IMPROVEMENT % DISTANCE RATIO CURVE

- 1 ●●● HALF CATHODES ON SAME SIDE OF ANODE IN THROWING POWER BOX
 4 ●●● ON OPPOSITE SIDES OF ANODE IN THROWING POWER BOX
 2 ●●● ON SAME SIDE OF ANODE IN LARGE PLATING TANK
 3 ○○○ ON OPPOSITE SIDES OF ANODE IN LARGE PLATING TANK



over the distance ratios were greater than when the half cathodes were on the same side of the cathode. This was due to screening of the remote half cathode by the near half cathode.

When the experiments were made in a vessel with a large cross-section in comparison with the area of the electrodes, the "improvement per cent." was much greater than when the cross-section of the vessel was equal to the anode area. This was due to screening in the latter case by the sides of the containing vessel, i.e., in the former case the lines of flow of the current could spread in a considerable volume, while

in the latter case they were confined to a rectangular channel of the same cross-section as the anode.

When the half cathodes were on the same side of the anode, both types of screening occurred.

When the throwing-power box is used for the determination of throwing power in the orthodox way the screening of one part of the cathode by another part is entirely avoided.

Throwing power determined by the Haring and Blum method is not

affected by screening of one part of the cathode by another part, but is affected by screening by the bath container in such a way that the "distance ratio" equals the "primary current ratio." Apart from utilising as standard a condition of screening very convenient for throwing power experiments, the Haring and Blum method has other advantages.

(1) The anode current density and the cathode current density are kept constant within narrow limits. If a sheet cathode is hung freely in a bath and plated, it is well known that more metal is deposited on the edges than in the middle. In the throwing-power box the deposition is more uniform over the whole surface of each half cathode as a result of screening by the sides of the box. In some baths, however, the thickness of deposit is not quite even owing to the depletion of cathions in the electrolyte causing an upward current of electrolyte in contact with the cathode, the former becoming more and more depleted of cathions until the surface of the bath is reached. This results in the deposit being slightly thicker at the bottom than at the top of the cathode.

(2) The throwing-power box forms a very satisfactory holder for the electrodes, maintaining correct adjustment and alignment. If an open bath is used and electrodes are suspended in it, conditions closely resembling those of actual practice are produced, and an indication of the throwing power of the bath is obtained. The method has disadvantages, however. In addition to screening of one part of the cathode by another part and uneven current distribution on each part of the cathode, it is not simple to position the electrodes accurately with respect to one another, and also with respect to the container of the bath. If the positioning is not accurate, consistent results cannot be obtained.

Conclusions.

When the half cathodes are both on the same side of the anode in the throwing-power box, there is marked screening of the remote half cathode by the near half cathode.

If the same electrodes are suspended in the same relative positions in a larger bath the current distribution is more favourable, but measurements of current distribution with the half cathodes on opposite sides of the anode indicate that in the former case there is still some screening of the remote half cathode by the near half cathode.

When there is no screening in a bath large compared with the size of the cathode, the primary current ratio is numerically smaller than the distance ratio. Screening tends to make the two ratios more nearly equal, or may in extreme cases make the primary current ratio greater than the distance ratio.

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STUDIES IN OPTICAL ACTIVITY. PART IV. RACEMISATION OF THE OPTICALLY ACTIVE OXALATES.

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Thirteen trivalent metal ions are known to combine each with three oxalate ions forming complex anions of the type $[M(C_2O_4)_3]^{---}$, of which nine belong to Transitional Groups of the Periodic Table. The most important are the following: $M = V, Cr, Mn, Fe, Ru, Co, Rh, Ir,$ and Al . Optical isomerism is definitely established in the cases of $Cr, Co, Rh,$ and Ir , alleged, though disputed, for Fe and Al , whilst the remainder have so far resisted attempts to resolve them.

The Magnetic Criterion.

In Part I. of this series ¹ attention was drawn to a similarity between the electronic structures of $Cr^{3+}, Co^{3+}, Rh^{3+},$ and Ir^{3+} in these oxalate compounds revealed by their magnetic susceptibilities which marks them off from the remainder. It was suggested that this distinction was related to the question of resolvability. Additional support for the hypothesis is furnished by Fe^{2+} and Pt^{4+} which, being diamagnetic ² in their optically active co-ordination compounds, ³ e.g. $[Fe(dipyridyl)_3]^{++}$ and $[Pt(en)(NH_3)(NO_2)(Cl)_2]^+$, possess completely analogous structures. The rare element ruthenium, homologue of iron, is particularly interesting for optical isomers of $[Ru(NO)(py)(C_2O_4)_2]^-$ have been prepared ⁴ and other ruthenium compounds of the same type, containing nitric oxide, are known to be diamagnetic.⁵ On the other hand, efforts to resolve $[Ru(C_2O_4)_3]^{---}$ proved fruitless; ⁶ the paramagnetic susceptibility of the ion is unknown but likely to be either one or five Bohr magnetons, and if the former, as seems probable, further attempts would be worth while.*

¹ Johnson, *Trans. Faraday Soc.*, 1932, **28**, 845.

² Bose, *Z. Physik*, 1930, **65**, 682; Berkman and Zocher, *Z. physik. Chem.*, 1929, **124**, 318.

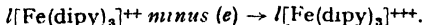
³ Werner, *Ber.*, 1912, **45**, 433; Chernyaev *Ann. inst. platine*, 1928, **6**, 23.

⁴ Charonnat, *Ann. Chim.*, 1931, **16**, 202.

⁵ Bose, *loc. cit.*, p. 681.

⁶ Charonnat, *loc. cit.*, p. 160.

* Of the numerous co-ordination compounds of ferric ion, Fe^{3+} , only ferri-cyanide, $[Fe(CN)_6]^{---}$, with one Bohr magneton, satisfies the magnetic criterion of resolvability, but the ion is structurally incapable of mirror-image isomerism. Very recently, however, Walden, Hammett and Gaines ⁷ have shown ferric tri-orthophenanthroline, $[Fe(o-phen)_3]^{+++}$, to be magnetically equivalent to ferri-cyanide. A year ago, F. T. Hamblin and the writer, having formed the same opinion regarding the probable magnetic susceptibility of the analogous blue ion $[Fe(dipyridyl)_3]^{+++}$, attempted to produce it in an optically active condition by direct oxidation of *lævo* ferrous tri-dipyridyl with chlorine, *i.e.*,



The experiment failed but this by no means rules out the possibility that the ion will eventually be resolved.

⁷ Abegg's *Handbuch der anorganischen Chemie*, 4; Abtlg. 3, Teil 2B; Lfg. 1; p 137, (1930).

⁸ *J. Chem. Physics*, 1935, **3**, 364

The peculiar virtue of this electron configuration in promoting optical isomerism lies in its high bonding energy. Cobaltic ion, for example, is enabled to pass from quintet multiplicity in the simple salts to a level having zero multiplicity when co-ordinated, a transition which would normally be endothermic. The fundamental criterion therefore is bond-energy which sometimes effects a change in magnetic susceptibility. The energy varies from compound to compound and complex ions frequently undergo racemisation in solution and, as will be shown subsequently, in the crystalline state.

The main purpose of this and succeeding papers will be to study the process of racemisation amongst optically active co-ordination compounds and to discover the various ways whereby molecular-ions lose their activity.

Review of Previous Work.

Considering that nearly twenty-five years have elapsed since Werner's spectacular discovery of optically active oxalates,⁹ the paucity of quantitative data is surprising.

TABLE I.

M.	$t_{\frac{1}{2}}$	Observer.
Cr	0.5 hours	Werner ; ⁹ Rideal and Thomas ; ¹⁰ Treadwell and co-workers ¹¹
Co	10 hours	Johnson and Bushra ¹²
Rh	∞	Werner ¹³ ; Jaeger ¹⁴
Ir	∞	Delépine ¹⁵ ; Jaeger ¹⁶
Al	(1) 50 hours (2) $\left[\begin{smallmatrix} 0.5 \\ 5 \end{smallmatrix} \right]$ hours $\left[\begin{smallmatrix} 1 \\ 22 \end{smallmatrix} \right]$ hours	Wahl ¹⁷ Burrows and Lauder ¹⁸
Fe	0.5 hours (?) 0.25	Treadwell and co-workers ¹¹ Thomas ¹⁹

Approximate times of half-change observed for the various complex ions in aqueous solution at room temperature are briefly summarised in Table I.

The compounds of rhodium and iridium are stable; at 100° C. there is slow diminution of rotatory power but it may be due to hydrolysis. There are no recorded data on cobaltioxalate, although Jaeger and Thomas²⁰ noted that the rate of racemisation was much slower than for chromioxalate. The consistent behaviour of chromioxalate in regard to racemisation provides a striking contrast to the strangely irregular results reported for the aluminium salt. A sample of $(\text{NH}_4)_3\text{d}[\text{Al}(\text{C}_2\text{O}_4)_3]$ prepared by Wahl took more than two days to lose half its rotatory power, whereas another preparation of the same compound commenced to racemise very rapidly, $t_{\frac{1}{2}} \approx 30$ minutes, but after about half an hour the rate slackened to an approximate final value of $t_{\frac{1}{2}} = 5$ hours. These fluctuations are indicated by square brackets in the Table.

⁹ *Ber.*, 1912, **45**, 3061.

¹⁰ *J.C.S.*, 1922, **121**, 196.

¹¹ Treadwell, Szabados and Haimann, *Helv. Chim. Acta*, 1932, **15**, 1040.

¹² *Unpublished*.

¹³ *Ber.*, 1914, **47**, 1954.

¹⁴ Jaeger, *Proc. Kon. Akad. Wet. Amsterdam*, 1918, **20**, 203.

¹⁵ *Bull. Soc. Chim.*, 1917, (4), **21**, 157.

¹⁶ *Ibid.*, 1919, **21**, 203.

¹⁷ *Ber.*, 1927, **60**, 399.

¹⁸ *J.A.C.S.*, 1931, **53**, 3600.

¹⁹ *J.C.S.*, 1921, **119**, 1140.

²⁰ *Proc. Kon. Akad. Wet. Amsterdam*, 1919, **21**, 603.

Wahl pointed out that the racemisation was evidently catalysed but made no further investigations. The later observations of Burrows and Lauder are similar in character. For example, in one experiment the racemisation of *tri*-strychnine *l*-aluminium-oxalate was initially faster in chloroform than the corresponding *d* compound in water whilst in another the rate was much slower. The figures in the Table refer to a particular experiment with $K_3dAl(C_2O_4)_3$. A recent contribution by Treadwell, Szabados and Haimann contains no relevant data but a statement that resolution of potassium aluminioxalate was achieved by Wahl's procedure and that the racemisation rate was similar to chromioxalate (*cf.* Wahl).*

Now although we have found the racemisation of potassium *chromi*-oxalate in solution strongly susceptible to catalytic influences (Part VI. of this series), the method used by every investigator to prepare the optically active compound yields an invariable product, as evidenced by concordant figures given in the literature for the rate of decay. Yet if we accept at its face value the data on the *more stable* aluminioxalate ($t_{\frac{1}{2}} = 0.5$ hours to 2 days), prepared in precisely the same way, we are forced to conclude either that two or more species of the molecular-ion exist possessing different decay-periods, or that a catalyst is produced *in situ* on the glass surface of the container or in distilled water and chloroform, which is specific to this compound and disappears during the course of racemisation.

It remains to say that up to the present, all attempts made in this laboratory to effect a resolution of $[Al(C_2O_4)_3]^{---}$ have been unsuccessful. The same remark applies to ferrioxalate ion. A summary paper by Delépine²² has recently appeared in which are described the results obtained by his powerful method of resolution, which depends upon the separation, from saturated solutions, of "active racemates" of the type $K_3d[M'(C_2O_4)_3]/[M''(C_2O_4)_3]$, M' and M'' being different metals. By this means were resolved the trioxalates of Cr, Co, Rh, and Ir. Parallel experiments with Al, Fe and Ru failed although mixed crystals of identical habit were just as readily produced. He therefore concluded that the rates of racemisation in solution were excessively rapid.

Theories of Racemisation.

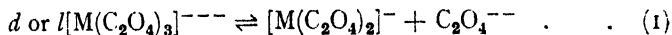
Werner expressed the opinion⁹ that chromioxalate ions lose their rotatory power through the momentary vacuation of *one* co-ordination position by an oxalate radicle, thus permitting an interchange of positions when it joins up again. As the oxalate ion is not supposed to be-

* Mention should be made of an investigation on co-ordination compounds of Al^{3+} carried out in this laboratory by R. V. Seddon and the writer. After several fruitless attempts to resolve $[Al(C_2O_4)_3]^{---}$, a new complex salt, tri-potassium aluminium malonate was prepared. (Found: Al, 5.40; C, 21.95; H_2O , 10.7. $K_3Al(C_3H_3O_4)_3 \cdot 3H_2O$ requires: Al, 5.36; C, 21.4; H_2O , 10.7 per cent.). Difficulties were encountered in applying the ordinary methods of resolution so the negative results are inconclusive. We also prepared potassium aluminium *tri*-catechol, originally described by Weinland and Denzel²¹ which Treadwell and co-workers¹¹ claim to have resolved, but our analytical data and the isolation of two sorts of crystals led us to doubt its supposed constitution. (Found for anhydrous material: Al, 4.7; C, 44.0; H, 2.8. $K_3Al(C_6H_4O_2)_3$ requires: Al, 5.78; C, 46.2; H, 2.56 per cent.) Aqueous solutions of the compound quickly turned black on the slightest exposure to air, so the work was abandoned. Treadwell and co-workers mention the tendency of solutions to darken but give no analytical figures. The alleged optical activity rests upon an observation of 0.05° .

²¹ *Ber.*, 1914, 47, 737.

²² *Bull. Soc. Chim.*, 1934, (5), 1, 1256.

come completely detached, the process can be conveniently referred to as racemisation by way of *intramolecular* change. Several other mechanisms suggest themselves which do not involve the breaking of even one bond but require activation energy and perhaps the participation of solvent molecules in order to effect the re-arrangement. An alternative theory proposed by Thomas¹⁹ assumes that an oxalate ion splits off from the complex, the residue undergoing re-orientation to a planar distribution of the four co-ordinated points, and when, finally, recombination occurs, the original configuration and its mirror image are formed with equal probability. Thus:



The experimental evidence adduced by Thomas and co-workers in support of "secondary ionisation" is of three kinds: (1) the precipitation of insoluble oxalates by certain positive ions, (2) measurements of electrical conductivity and electrode potential, (3) influence of solvent upon the rate of racemisation.

According to Thomas¹⁹ "... the complex oxalates of iron, chromium and cobalt react with dilute silver nitrate with the formation of silver oxalate. The ferri complex which racemises with great rapidity gives immediately a dense white precipitate. The chromic salt produces a precipitate on keeping." As a matter of fact the precipitate which forms immediately on adding silver nitrate to potassium ferrioxalate is not white and when dissolved in acids gives rise to yellow solutions. Calcium chloride also produces a yellow precipitate but, be it noted, more slowly and in smaller quantity. Cold dilute solutions of potassium *d* chromioxalate and silver nitrate can be mixed and left for many hours without visible change, but when precipitation ultimately occurs the product consists largely of coloured crystals. These were identified by Kistiakowsky²³ as $\text{Ag}_3\text{Cr}(\text{C}_2\text{O}_4)_3 \cdot 6\text{H}_2\text{O}$. Crystalline salts of the type $\text{K}_n\text{Ag}_m\text{M}(\text{C}_2\text{O}_4)_3 \cdot x\text{H}_2\text{O}$, where $m+n=3$, $\text{M}=\text{Co}, \text{Rh}$, etc., have been prepared in this fashion by several experimenters.²⁴ We have also proved conclusively that *positive ions disintegrate chromioxalate ions*. With a few interesting exceptions, monovalent cations do not exert pronounced effects, but the rate of destruction increases with the valence number of the ion, with concentration and temperature. The disintegration of co-ordination compounds of *chromium* is particularly easy to follow with a spectroscope (*cf.* Johnson and Mead),²⁵ though doubtless it happens in other cases too. The matter will be dealt with in a subsequent communication. For present purposes, the important inference is that the slow precipitation of insoluble oxalates, even when it occurs, is not a reliable criterion of "secondary ionisation" such as depicted in equation (1).

Thomas's conductivity data on solutions of potassium chromioxalate at concentrations comparable with those used by him for measurements of the rate of racemisation, imply appreciable decomposition of the molecular-ion into Cr^{3+} and $3\text{C}_2\text{O}_4^{--}$, a result compatible only with *instantaneous racemisation*. On the other hand the earlier work of Kistiakowsky²³ supports the view that no measurable decomposition of the complex ion occurs even in extremely dilute solution. Thomas and Fraser²⁶ attempted to estimate the concentration of free oxalate ions

¹⁹ *Z. physik. Chem.*, 1890, **6**, 97.

²⁴ Kranig, *Ann. Chim.*, 1929, **11**, 44; Jaeger, *Rec. Trav. Chim.*, 1919, **38**, 268.

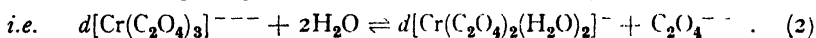
²⁵ *Nature*, 1933, **131**, 399.

²⁶ *J.C.S.*, 1923, **123**, 2973.

by means of silver electrodes dipping into solutions of the complex salts saturated with silver oxalate. We have been unable to verify their results. Finally, the postulate of secondary ionisation is said to receive support from the fact that addition of acetone to an aqueous solution of chromioxalate diminishes the rate of racemisation (*cf.* Werner),⁹ at the same time increasing the absorption coefficients and greatly broadening the absorption band in the visible spectrum. We have confirmed the retarding influence of acetone but *not* the alleged alteration in the spectrum. Possibly the absorption coefficients are slightly augmented but the amount both in the visible and in the ultra-violet is too small to assert with confidence.

Now even if some kind of ionisation mechanism is in fact responsible for racemisation, it is highly improbable that the dissociation could be detected by ordinary chemical and physico-chemical means, *for if secondary ionisation was thus capable of proof the rates of racemisation would be practically infinite.* And it is significant that the presence of oxalate ions can no more be demonstrated in aqueous solutions of pure ferric, aluminium, or ruthenium²⁷ trioxalates than in the cases of chromium or cobalt which racemise at measurable rates.

The simple scheme illustrated in equation (1) takes no account of the solvent, whereas under the conditions of observation the assumed re-arrangement to a planar configuration is likely to be forestalled by the entry of two water molecules (in place of the discarded oxalate ion) or an oxalate ion, or possibly by these two events in succession. Thus, racemisation is perhaps slower than the dissociation process,



These considerations are important because they afford opportunities of distinguishing broadly between the theory of secondary ionisation and the theories of intramolecular re-arrangement. For Werner and co-workers²⁸ claim to have prepared crystalline compounds of both *cis* and *trans* $[\text{Cr}(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_2]^-$ and consequently their absorption spectra and, for example, the manner and rates of reaction with oxalate ion can be investigated.

Turning once again to the alternative hypothesis of intramolecular change, we shall bring forward in this and succeeding papers several instances of racemisation occurring in crystals. In such cases the usual concept of ionisation is without significance, and if this can happen in crystals there is no apparent reason why intramolecular rearrangement should not take place in a liquid medium.

Racemisation of Tri-Potassium *d* and *l* Chromioxalates in the Crystalline State.

Optically active potassium salts are prepared from the corresponding tri-strychnine salts (Part V) by trituration with excess of aqueous potassium iodide which precipitates insoluble strychnine iodide, followed by addition of alcohol to the filtrate. The powder which separates cannot be re-crystallised from water on account of the rapid rate of racemisation, and the potassium salts are not soluble in any other pure liquid. They can be reprecipitated from ice-cold water, but only with considerable loss of rotatory power. Several different preparations have been analysed for water with results ranging from 7.0 to 8.2 per cent. ; $\text{K}_3\text{Cr}(\text{C}_2\text{O}_4)_3 \cdot 2\text{H}_2\text{O}$ requires

²⁷ Charonnat, *loc. cit.*,⁴ p. 158.

²⁸ *Ann. Chem.*, 1914, 406, 261.

7.7 per cent. H_2O . Thus the optically active potassium chromioxalates fall into line with those of cobalt²⁰ and iridium²² which also crystallise with two molecules of water.

Partial racemisation takes place when the substance is kept at room temperature in stoppered bottles in the dark. No significant amount of water is taken up during the process. The behaviour varies somewhat from sample to sample but, so far, controlled experiments on the possible effect of fluctuations in room temperature, of the glass surface of the containers and alterations in the treatment of the powder after preparation have failed to discover any specific influences. Generally speaking, a slow diminution of rotatory power during the first few weeks (or perhaps months) is followed by a relatively rapid phase which finally comes to an end even though between 15 and 30 per cent. of the original rotatory power is retained. Later, reaction may start again. The observations in Table II. refer to a particular sample of $\text{K}_2\text{Cr}(\text{C}_2\text{O}_4)_3 \cdot 2\text{H}_2\text{O}$.

Another preparation which originally contained at least 50 per cent. of racemate showed nothing unusual in its behaviour so the presence of racemic crystal nuclei does not seem to be important. Partially racemised material is distinctly greener in appearance than the freshly resolved substance, the colour of which cannot accurately be described although some have called it "purple."

TABLE II

Time from Date of Preparation (Days).	Observed Rotation.
0	$\cdot 86^\circ$
21	$\cdot 76^\circ$
66	$\cdot 43^\circ$
184	$\cdot 26^\circ$
234	$\cdot 25^\circ$
345	$\cdot 25^\circ$
462	$\cdot 05^\circ$

TABLE III.

Time from Start (Days).	Observed Rotation.	
	16°C	115°C .
0	$\cdot 61'$	$\cdot 61'$
38	$\cdot 47'$	$\cdot 62'$
87	$\cdot 41'$	$\cdot 53'$

In order to find out whether the rate of racemisation is susceptible to thermal activation, some dextrorotatory salt was taken and divided into two portions; one was kept at room temperature in the usual manner and the other placed in an air oven. After a few hours, the stopper of the weighing bottle containing the heated sample was inserted; otherwise, no special precautions were taken to prevent contact of the solid with moist air. The heat treatment was continued for almost *three months* at an average temperature of 115°C . The rather striking results are summarised in Table III.

It is clear that the process of racemisation proceeds faster and further in the hydrate at room temperature than in the anhydrous substance at 115°C . It should be borne in mind, too, that the conditions of experiment at high temperature did not totally exclude water vapour. The desiccated salt can be kept *in vacuo* over phosphoric oxide at room temperature for three weeks (experiments of longer duration have not yet been attempted) without significant loss of activity.

Relatively few experiments have been carried out with



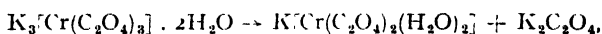
but one preparation which originally gave a rotation of 0.85° fell to 0.28° after seventeen months. Heating the freshly prepared salt for two days

²⁰ Johnson and Mead, *Trans. Faraday Soc.*, 1933, **29**, 626.

at 115° C. in an open vessel caused no measurable alteration in rotatory power.

Polarimetric observations were made by dissolving approximately 0.01 gr. of potassium chromioxalate in 25 c.c. of aqueous acetone (40 per cent. acetone by volume), in which solvent the rate of racemisation is very slow, and examining the solution in a 15 cm. tube with the aid of a sodium vapour lamp. The routine for a given sample of material was of course standardised, but the rotations cited for various preparations are not comparable one with another.

A different type of experiment has been found to give results of interest. When *d* or *l* $K_3Cr(C_2O_4)_3 \cdot 2H_2O$ is heated at 120° C. in evacuated sealed tubes of sufficient capacity to discount any possibility of condensation of liquid water, complete racemisation occurs within twelve hours. Thus the presence of a small quantity of water vapour will bring about in a short space of time that which months of heating fails to produce in the dry solid. There are indications that the course of racemisation in these circumstances is similar to that observed at room temperature; *i.e.*, an induction period followed by rapid reaction, which, however, proceeds to completion; but it will be necessary to improve the experimental technique before a definite conclusion can be reached. The racemate is green but the absorption coefficients of its aqueous solution are perfectly normal and chemical tests failed to detect the presence of potassium oxalate. The following reaction is therefore eliminated:—



and moreover a diaquo di-oxalate has been prepared and its properties do not correspond. Further discussion is reserved until the final paragraph.

Racemisation by Precipitation.

Precipitation by addition of absolute alcohol is the recognised method for recovering optically active potassium salts from aqueous solution. It was noticed in the case of *d*-chromi-oxalate that repeated precipitation resulted in very considerable loss of activity; indeed, four reprecipitations sufficed to produce a racemic solid. Now the filtrates remaining after precipitation were found to give higher dextrorotations per unit quantity of dissolved salt than the corresponding solid residues, which proved the racemate to be less soluble than its optically active components. But even when allowance is made for this, a nett loss of rotatory power amounting to about 15 per cent. of the original (sometimes more, sometimes less) remains unaccounted for,

$$i.e., \quad \alpha_o > (1 - x)\alpha_r + x\alpha_f.$$

x is the fractional amount of substance in the filtrate and α_o , α_r , α_f the rotation for the D line of sodium of the original material, residue and filtrate respectively, reckoned for a solution containing 0.01 gr. in 25 c.c. of solvent in a 15 cm. tube.

The experimental procedure was as follows: 0.7 gr. of dextro potassium salt was quickly dissolved in 10 c.c. of ice-cold water and immediately precipitated by cautious addition of 20 c.c. of ice-cold absolute alcohol with stirring. The temperature was observed to rise to 6° C. and about 90 per cent. of the salt was re-precipitated under these conditions. The rate of racemisation is very slow in aqueous alcohol (1:2 by volume) and since the compound is only in solution for about a minute at an average temperature of 3° C. the consequent loss of activity is negligible. By carefully recording the time required for each operation and by following the course

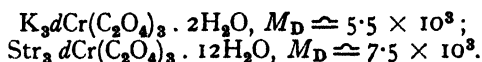
of racemisation of the filtrate, an accurate estimate of its initial rotatory power can be made. The salt content of the filtrate is then determined and hence α . The data obtained in one experiment are given in Table IV.

TABLE IV.

	Weight. w.	α .	$\Sigma\alpha$.
Starting material .	0.708 gr.	0.73°	0.52
Precipitate .	0.64 gr.	0.53°	0.42
Substance in Filtrate .	0.07 gr.	1.1°	

Since the presence of alcohol in water does not appreciably affect the absolute rotatory power at 5893 Å., it appears that the process of precipitation results in partial racemisation.

Presumably the act of solution may also be accompanied by loss of activity but this obviously cannot be proved. Therefore it is impossible by the recognised method to prepare optically pure potassium *d* chromi-oxalate from the strychnine salt, even though the latter were perfectly resolved. Our most active solids have been found to possess much smaller mol.-rotations than the parent alkaloid salts, e.g.,



In the case of *cobalti*-oxalate, just the reverse has been observed.²⁹ This might be anticipated since the slower rate of racemisation of the potassium salt in water implies a greater stability, but an additional complication enters on account of the racemising propensities of crystalline strychnine *d* and *l* *cobalti*-oxalates.

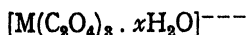
Clearly the phenomenon is likely to become more and more important as the tendency to racemise increases and must be taken into consideration when designing new methods of resolution for the more intractable oxalates.

The Function of Water in Trioxalate Compounds.

The essential participation of water in promoting racemisation in crystalline potassium *d* and *l* *chromi*-oxalates is evident from the foregoing account. At room temperature one may suppose that invasion of the complex ions by water molecules occurs with consequent rearrangement and loss of rotatory power. Possibly an "expansion" accompanies the process, together with a loosening of the bonds uniting oxalate to metal. Transitorily, at any rate, some of the water of crystallisation plays a more important rôle and may be regarded as water of composition. A more precise statement cannot be made until further experiments have been carried out. To what extent the lattice constraints are responsible for maintaining the configuration of the molecular-ions is uncertain, for although the desiccated potassium salts seem to retain their optical activity indefinitely, the anhydrous strychnine salts undergo racemisation (Part V.). The compounds cannot be vaporised and the fact that measurements of rotatory power have been made by dissolving the salts proves nothing since the solvent may likewise exert a restraining influence. Some observations on the racemisation of *tri*-strychnine *chromi*- and *cobalti*-oxalates in water suggest that the rates are slower at 18° C. than

for the corresponding potassium salts. Positive ions therefore appear to exert specific influences in solution, whilst in the crystalline state their varying "sizes" would be expected to operate still more significantly by controlling the characteristics of the lattice.

The water in all these compounds, including the partially racemised substances, is quickly and completely removed *in vacuo* over phosphoric oxide at room temperature, so the bonds of union are weak. It would be misleading to represent the aquo-ions by formulæ such as



because water inside Werner's bracket is very firmly attached. For example, $K[Cr(C_2O_4)_2 \cdot 2H_2O]$ can be heated for many hours at $130^\circ C.$ without loss of weight. It must be admitted, however, that when the co-ordination number is greater than six, as in the above formula, an element of doubt remains regarding the ease of removal of water.

In this connection a very comprehensive Thesis published in 1931 by Charonnat contains a suggestion of great interest.³⁰ As an alternative to Werner's octahedron, he proposed a cubic configuration for *tri*-oxalates, placing a water molecule at each of two diagonally opposite corners and oxalate radicles along three edges. The model possesses the same kind of symmetry as Werner's and is *equally satisfactory for the purpose of explaining optical isomerism*, which was the point Charonnat chiefly wished to make. The evidence submitted in support of it is extremely slender and open to criticism; the most suggestive being that the optically active oxalates of Cr, Co, and Ir crystallise with two molecules of water, though at the time when the idea was put forward the hydration data were conflicting. However, the present writer was led quite independently to adopt similar but less precise notions as a result of experiments on racemisation.

We³¹ have recently resumed the study of *cobalti*-oxalates and have confirmed the remarkable racemising properties of the crystalline strychnine salts.²⁹ There is no doubt that progressive changes take place in the hydrated crystals at ordinary temperatures immediately after preparation, for the rotatory power and absorption spectra undergo marked alteration on keeping, even in the dark. These changes do not appear to be caused by reduction of Co^{3+} to Co^{2+} nor is water gained or lost by the crystals. Contrary to a previous statement,³² it is impossible to remove water from the strychnine *cobalti*-oxalates without causing decomposition ($Co^{3+} \rightarrow Co^{2+}$) which thereafter proceeds practically to completion in the anhydrous solids. The *d* salt which contains more water than the *l* decomposes at a greater rate. The strychnine salts ($d \rightleftharpoons 12H_2O$; $l \rightleftharpoons 8H_2O$) undergo rapid decomposition at $85^\circ C.$ whereas the racemic potassium salt ($3.5 H_2O$) only slowly turns pink at $110^\circ C.$

All these facts suggest that water makes a significant contribution to the properties of cobalti-oxalate ion.

Wyruboff³³ claims that anhydrous ferrioxalates are not light sensitive, in striking contrast to the hydrated salts.

³⁰ Charonnat, *loc. cit.*,⁴ p. 150.

³¹ E. Bushra and the writer, *unpublished*.

³² Johnson and Mead, *loc. cit.*,²⁹ p. 630.

³³ *Bull. Soc. franc. Minéral.*, 1900, **23**, 65.

Summary.

The properties of metallo-trioxalates are discussed with particular reference to optical activity and racemisation, as representing one of the most important classes of co-ordination compounds. Two theories of the racemisation process can be broadly distinguished: (1) ionisation, (2) intramolecular rearrangement. The experimental evidence hitherto accepted as supporting the theory of "secondary ionisation" is shown to be unreliable and based upon a misconception. For even if ionisation was responsible for loss of rotatory power it could not be demonstrated by ordinary chemical or physico-chemical methods in the cases of compounds which racemise at *measurable* rates. On the other hand, the newly discovered phenomenon of racemisation of chromi- and cobalti-oxalates in the *crystalline* state is a strong indication that intramolecular rearrangement takes place; and if possible in crystals, is equally likely to occur in a liquid solvent medium. *There is evidence that water molecules play an important part in determining the properties of these oxalates.*

A supplementary discussion of the connection between magnetic susceptibility and optical isomerism is given, and a brief account of some co-ordination compounds of aluminium.

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PART V. RACEMISATION OF THE STRYCHNINE SALTS OF DEXTRO AND LÆVO CHROMI-OXALATE IN THE CRYSTALLINE STATE.

By C. H. JOHNSON AND A. MEAD.

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The separation of racemic chromioxalate and cobaltioxalate ions, $dl[Cr(C_2O_4)_3]^{---}$ and $dl[Co(C_2O_4)_3]^{---}$ into dextro and lævorotatory components is easily effected by fractional crystallisation of the strychnine salts,¹ from which optically active potassium salts can be prepared. It is well known that these substances gradually lose their optical rotatory power when dissolved in water, but we have discovered that under certain circumstances they also racemise *in the crystalline state*. Unmistakable evidence of the phenomenon was first obtained with *tri*-strychnine *l* cobaltioxalate which suffered almost complete racemisation in the course of a few weeks at room temperature.² Crystalline *tri*-strychnine *d* cobaltioxalate was likewise found to undergo partial racemisation. The bright green crystals remained unaltered in appearance and there were no signs of decomposition. However, on account of the instability of cobaltioxalates towards heat and light, it was thought advisable to transfer attention for the time being to the stable chromioxalates.

¹ Werner, *Ber.*, 1912, **45**, 3061; Jaeger and Thomas, *Proc. Kon. Acad. Wet. Amsterdam*, 1919, **21**, 693; Jaeger, *Rec. Trav. Chim.*, 1919, **38**, 171.

² Johnson and Mead, *Trans. Faraday Soc.*, 1933, **29**, 626.

Tri-strychnine *d* chromioxalate is readily obtained in large quantities and most of the experiments about to be described were made with this compound. It was soon established that the crystals do not racemise at ordinary temperatures, and *tri*-potassium *d* chromioxalate prepared from it can be heated in an open vessel at 120° C. for two days without appreciable loss of rotatory power. We were therefore surprised to find that partial racemisation of the strychnine salt occurred on heating, and to an extent dependent on the temperature, being more complete the higher the temperature, though never quite complete even after prolonged exposure at 130° C. The next discovery of note was that racemisation takes place in the desiccated solid at room temperature when the crystals are dehydrated by phosphoric oxide *in vacuo*. This is illustrated in Fig. 1. In order to ascertain whether size of particles is an important consideration, a representative sample of crystals was divided in two, one half finely powdered in an agate mortar, and both placed in the same vacuum desiccator. Determinations of rotatory power were made at intervals over a period of three weeks. The time required for complete removal of water is indicated by an arrow. A number of experiments has shown that curves

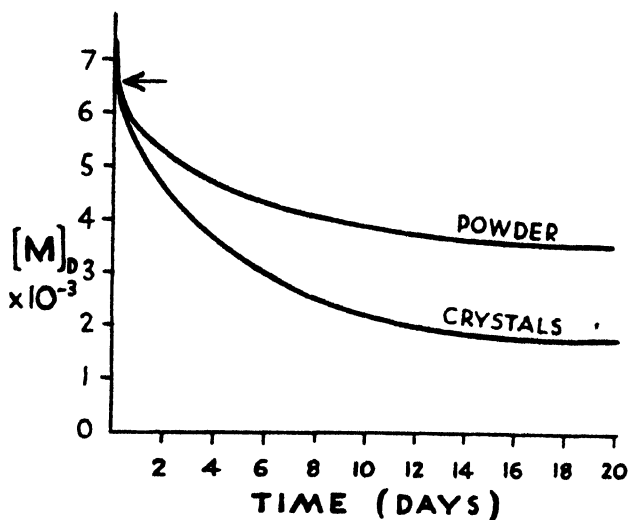


FIG. 1.

1 and 2 are only moderately reproducible, and the difference between them is not always so manifest as in Fig. 1. The significance of these results will be discussed later on.

It was essential to make sure that the process of racemisation was not actually one of decomposition, and this was established by the follow-

ing experiments. Strychnine chromioxalate which had been partially (say 80 per cent.) racemised by heating for several days at 110° C. was found to be *completely* soluble in chloroform, whereas decomposition must have resulted in the production of inorganic compounds insoluble in chloroform. Controlled tests with calcium chloride reagent proved the absence of potassium oxalate in the racemised substance. Finally, quantitative measurements were made of the absorption spectra of optically active (*d* and *l*) and racemised strychnine chromioxalates dissolved in chloroform. The spectra were identical as regards the position of maximum absorption, approximately 5700 Å., and the molecular absorption coefficients checked within 4 per cent., the limit of accuracy of our Nutting Photometer. Clearly, therefore, racemisation is neither the result of, nor is it accompanied by, decomposition of the molecular-ion. Furthermore, *tri*-strychnine *l* chromioxalate, the isomer of opposite sign to that of the starting material, was obtained in large quantities by slow crystallisation of the racemised compound from chloroform.

Results.

Tri-strychnine *d* chromioxalate.— $\text{Str}_3[\text{Cr}(\text{C}_2\text{O}_4)_3] \cdot 12\text{H}_2\text{O}$ is prepared in the form of small flaky orthorhombic crystals, the water content being in the neighbourhood of 14 per cent. by weight. The act of pulverising the crystals is sometimes attended by the loss of about half a per cent. of water. Analytical data obtained with different samples are given herewith:—

Water	14.10	14.45	14.05	14.00	14.50 per cent.
Strychnine	67.0	66.4	66.9	66.7	per cent.

$\text{Str}_3[\text{Cr}(\text{C}_2\text{O}_4)_3] \cdot 12\text{H}_2\text{O}$ requires: H_2O , 14.05 per cent.; strychnine 65.5 per cent. Slightly high values for strychnine are invariably obtained by the direct analytical method.*

The keeping quality of the dextrorotatory salt is attested by Table I. It will be noted that the observed rotation of the crystals is sensibly unaffected by grinding in an agate mortar and that the powder likewise retains its rotatory power over long periods of time at room temperature. The standardised method of observation will be mentioned later on.

TABLE I.

Sample.	Date.	Powder.	Crystals.
A	2.6.33	$^{\circ}53$	$^{\circ}535$
	30.10.34	$^{\circ}535$	—
	20.6.35	$^{\circ}54$	—
B	19.3.34	$^{\circ}61$	$^{\circ}61$
	7.11.34	$^{\circ}60$	—
	20.6.35	$^{\circ}595$	$^{\circ}62$

The manner of racemisation at a number of different temperatures between 50° and 100°C . is depicted in Fig. 2. Details are given in the experimental section. It is particularly noteworthy that at a given temperature different preparations gave identical results, within the limits of accuracy of measurement, which were also unaffected by preliminary fine powdering of the crystals. In Fig. 2, the molar rotations refer to *d*-chromioxalate ion, allowance having been made for the small negative contribution of *l*-strychnine. Some features common to all the curves are apparent. An initial rapid rate of racemisation is succeeded by relatively slow rate at a level which is lower the higher the temperature. Curves of dehydration are also included in Fig. 2, which must be regarded as approximate. Obviously the bulk of the water is expelled some time before the rapid rate of racemisation comes to an end. The amount of

water quickly lost increases progressively with rise in temperature.

As already mentioned the course of racemisation at room temperature (P_2O_5) is influenced to some extent by powdering the crystals. A fairly good check on the curves of Fig. 1 was obtained with another sample of

TABLE II.

Time from Start.	Crystals.		Powder.	
	Per Cent. Loss of H_2O .	$[\text{M}]_D \times 10^{-3}$ Observed.	Per Cent. Loss of H_2O .	$[\text{M}]_D \times 10^{-3}$ Observed.
0	0	7.55	0	7.15
0.5 hrs.	85	7.20	94	6.45
1.3 hrs.	90	6.95	97	6.25
3.5 hrs.	97	6.25	100	5.75
18 hrs.	100	5.40	100	5.30
1 day 16 hrs.	100	4.55	100	4.60
6 days 7 hrs.	100	3.25	100	3.70

strychnine *d* chromioxalate, but in a third trial with crystals and powder of different preparations the rate of racemisation of the crystalline salt was not appreciably faster than for the powder until more than a week

had passed. A final experiment (Table II) was made, paying particular attention to the early stages; here again the crystals and powder were different preparations.

At the start the powder racemises faster than the crystals because it dries quicker. Afterwards the process in the crystals catches up and finally overtakes the other. There is little doubt that the ultimate amount of racemisation is generally greater for crystals than for powder, but it is also in the later stages that our results show the widest variability. It seems wise to postpone discussion of the phenomenon until the source of these fluctuations has been located, since the two are probably connected.

Tri-strychnine *l* chromioxalate.—The method used for the preparation of the *laevo* salt was slow fractional crystallisation of heat-race-

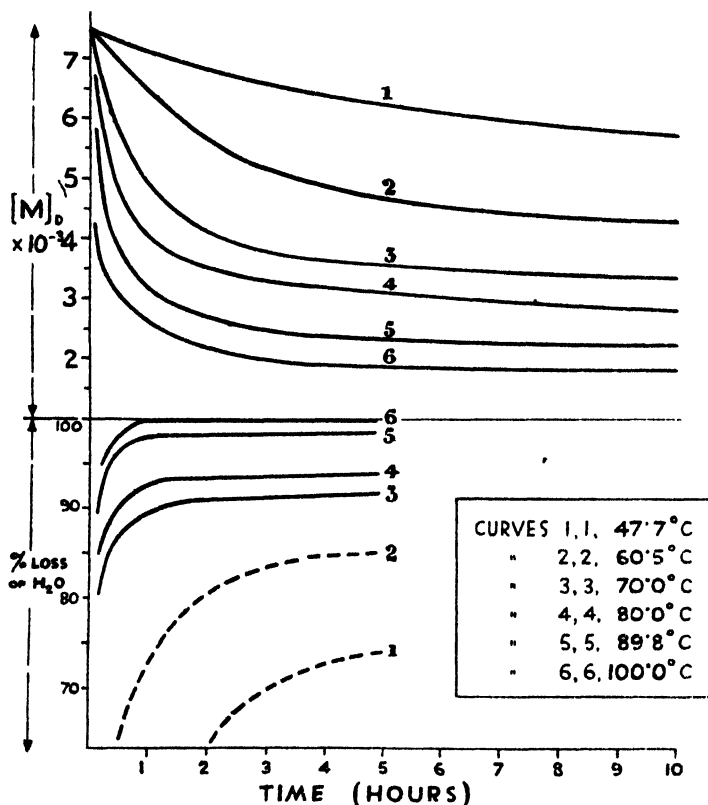


FIG. 2.

mised dextro-compound from chloroform. The large, well-formed red crystals which first separate are generally *laevorotatory*. They can be preserved in chloroform vapour but in air rapidly lose about half their weight, due to the escape of chloroform by crystallisation, and with it their transparency. The formula $\text{Str}_3 \cdot l[\text{Cr}(\text{C}_2\text{O}_4)_3] \cdot 12\text{CHCl}_3$ is not improbable but water is also present and analyses of three different preparations gave 4.8, 5.5 and 5.3 per cent.; $\text{Str}_3 \cdot l[\text{Cr}(\text{C}_2\text{O}_4)_3] \cdot 4\text{H}_2\text{O}$ requires 5.17 per cent. H_2O . The close correspondence between the molar rotations of the *d* and *l* compounds suggests that resolution is almost perfect. The values are higher than those previously reported for chromioxalate.¹ A correction must be applied for the contribution of *l* strychnine. Data obtained with our best resolved samples are given in Table III. Perhaps the slightly smaller

rotatory power of *l* chromioxalate is due to racemisation accompanying the evaporation of chloroform from the crystals.

At present the racemising properties of the *laevo* compound have merely been studied qualitatively, but two facts have emerged, namely that the loss of rotatory power caused by dehydration over phosphoric oxide *in vacuo* is much smaller than in the case of the *d*-salt, and the course of racemisation followed at 115° C. is similar to that of the *d*-salt at about 70° C.

Another point of contrast is the clear evidence that racemisation of the *l*-compound occurs when stored in stoppered bottles at room temperature. Two examples are given in Table IV.

TABLE III.

Salt.	$[M]_D \times 10^{-3}$ Observed.	$[M]_D \times 10^{-3}$ Corrected.
Dextro .	7.35	7.60
Lævo .	- 7.60	- 7.35

TABLE IV.

Sample.	Date.	Rotation (observed).
A	12.5.33	- .55°
	13.7.33	- .39°
	30.10.34	- .33°
B	6.5.34	- 1.14°
	21.10.34	- .78°
	20.6.35	- .70°

It should be emphasised that the divergent behaviour of the *d* and *l* compounds is doubtless due to differences in crystal structure and composition imposed by the methods of preparation. We have recently found a means of isolating the *laevo* salt from *aqueous* solution, which should assist in future investigations.

Analysis of Curves.

A simple exponential relationship between rotatory power and time cannot be fitted to the curves as they stand. In every case the final

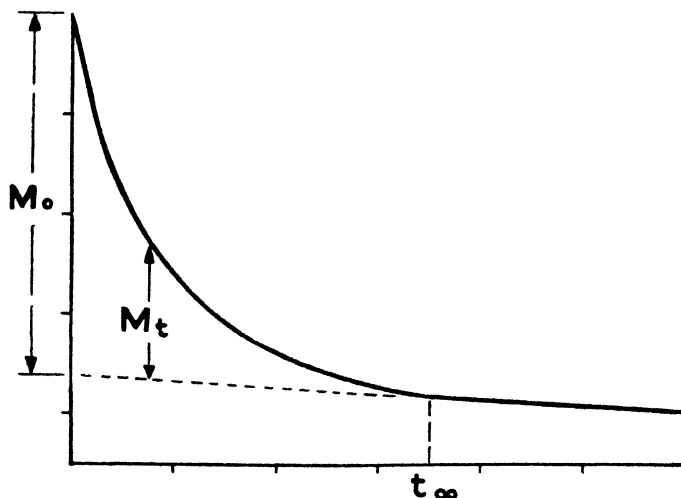


FIG. 3.

phase of racemisation is so slow that for a few hours at least there exists an approximately linear dependence of $[M]_D$ upon t . When this is

eliminated by the simple procedure illustrated in Fig. 3, the applicability of the equation $M_t = M_0 e^{-kt}$ to the fast phase can be tested by plotting $\log M_t$ against t . Three cases are shown in Fig. 4; (a) refers to 60°, (b) to 80°, and (c) to 100° C.

Curve (a) is linear from the commencement and remains so for 4 hours when gradual transition to the slow phase occurs. In curve (b),

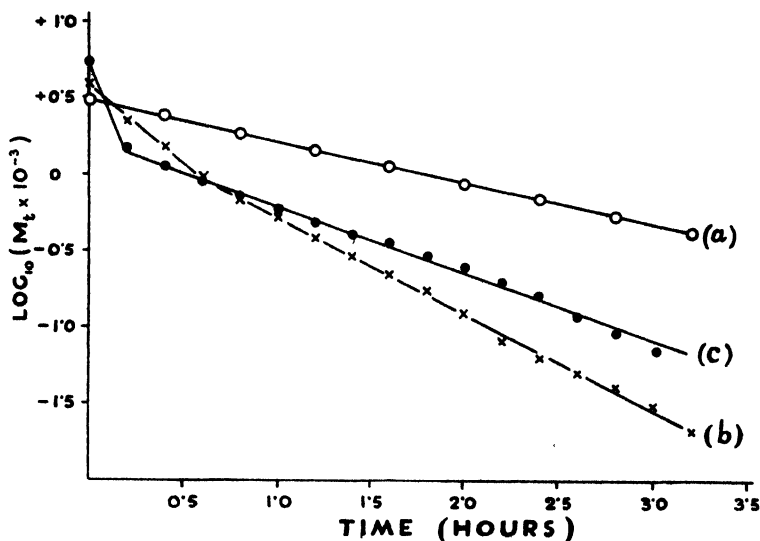


FIG. 4.

an initial steep slope is followed by a linear section lasting 2.5 hours. At 48° C. the graph is similar to (a), but persists longer (> 8 hours) and the slope is gentler. Curve (b) is representative of all temperatures above 60°, the initial decrement being more pronounced and more abrupt (*cf.* curve (c)) the higher the temperature. The main results

of the analyses are summarised in Table V.

TABLE V.

T° C.	$M_0 \times 10^{-3}$	$k \times 10^4$ (Moles./sec.).	t_∞ (Hours).
48°	2.0	0.37	> 8
60°	3.0	1.8	6
70°	3.6	3.2	3.5
80°	3.9	4.1	3.5
90°	4.9	3.2	3.5
100°	5.4	2.7	3.5

M_0 is a measure of the diminution of rotatory power which occurs during the *fast phase* of racemisation. At 48° it amounts to about 25 per cent. and at 100° to 70 per cent. of the total rotatory power of *d* chromioxalate ion. It is interesting to find that at and above 70° the velocity

constants k are approximately equal for the second stage of the fast phase which comes to an end (t_∞) some three and a half hours after the commencement of the experiment. No definite pronouncement regarding the initial decrement can be made at present, neither do our experimental data permit an accurate analysis of the *slow phase*. Assuming exponential functions for the latter, k is of the order 3×10^{-6} for the first few hours, *i.e.*, about a hundred times less than the fast rate. At 100°, k is appreciably smaller. It is quite evident, however, from measured rotations

that the ultimate rates of racemisation are practically zero. At 100° $[M]_D \times 10^{-3} = 1.95$ after 19 hours, whereas in 16 days it only fell to 1.05.

Because of the somewhat inconsistent results obtained in eight experiments at room temperature (P_2O_5) it was only possible to make rough analyses of the curves. They are definitely of type (b) for both crystals and powder. A relatively rapid phase of racemisation lasting a few hours is succeeded by an approximately exponential decrement, $k \approx 2 \times 10^{-6}$ moles per second, over a period of two or three weeks. After this, the process virtually ceases although as much as 35 per cent. of the original activity may be retained by powdered material.

Experimental.

Tri-strychnine *d* chromioxalate is prepared as follows: cold aqueous solutions of potassium chromioxalate ($\approx 0.25 M$) and nearly saturated strychnine sulphate are mixed in equivalent proportions. The precipitate, which contains an excess of the less soluble $Str_2 d[Cr(C_2O_4)_3]$, is put aside and the filtrate allowed to stand for a few hours. Racemisation occurs and consequently dextro salt crystallises out. A further quantity is obtained by surrounding the filtrate with ice. The molar rotation (*i.e.*, rotation per 10 cm. length \times molecular weight \div percentage composition by volume) at 5893 Å. of the product dissolved in chloroform is $6.85 \pm 0.5 \times 10^3$. Attempts to improve upon the value 7.35×10^3 by subsequent treatment of the crystals have failed.

The relative solubility of the *d* and *l* compounds is reversed in chloroform, and use has been made of this in isolating the *laevo* salt. Werner¹ prepared *di*-strychnine potassium *l* chromioxalate but, as far as we know, the *tri*-strychnine *l* chromioxalate has not previously been described.* The precipitates put aside during the preparation of the *d*-compound are almost completely racemised by repeatedly moistening with water and heating at $110^{\circ} C.$; then shaken up and left in contact with chloroform for several hours before filtering. The filtrate is allowed to evaporate very slowly at room temperature, when large red transparent crystals separate from solution. Relevant properties of the *l*-salt are referred to in a previous section.

The heating experiments were conducted in the following manner. Approximately 0.065 gram of strychnine salt was weighed out into each of several small cylindrical glass specimen-tubes which were placed, without stoppers, in an air-oven. These were removed from time to time, singly or in pairs, and the rotation determined by dissolving in 25 cc. of chloroform, a solvent in which the rate of racemisation is extremely slow. All measurements were made with an 8 cm. polarimeter tube and a sodium vapour lamp as the source of illumination. Rotations ranged from about 1° downwards and could be estimated to $\pm 0.01^{\circ}$.

The thermostat consisted of a copper oven ($1' \times 1.5' \times 1'$) lagged with 3 ins. of slag wool and enclosed in a wooden box. The heating circuit was in two parts, the main current being controlled externally by means of a rheostat, so that heat losses were nearly *but not quite* compensated at the working temperature. The second part of the heating circuit was furnished by a small wire grid fixed near the roof *inside* the oven, actuated by a regulator and mercury relay. A powerful fan maintained a thorough cir-

* A contrary statement is to be found in a recent text-book by T. M. Lowry, F.R.S., entitled *Optical Rotatory Power* (Longmans Green & Co., 1935), p. 85, but this is due to a departure from the usual sign convention; *d*-chromioxalate is called *l* and vice versa, an error which is traceable to Werner's original paper.¹ Werner made his observations with blue light on the *short* wave length side of the active absorption band.

culatation of air and the temperature could be held constant to $\pm 0.1^\circ$ for long periods of time.

A "cruet" was designed to carry the specimen tubes consisting of two circular brass discs, 19 cms. in diameter, rigidly fixed together 2 cms. apart by means of a hollow tube soldered to the centre of each, and projecting about 1 cm. through the lower one. Round the peripheries twenty holes were punched to accommodate the specimen tubes, the holes in the upper disc being concentric with those in the lower. The bottles rested upon, and when caused to do so, slid over an asbestos mat on the oven floor. Through the floor passed a spindle engaging with the central hollow tube which could be rotated by hand from underneath the box. Rotation of the cruet brought each bottle in turn over a vertical shoot down which they fell a distance of 2 ins., the fall being broken by a wad of cotton wool in a metal cup held in place by a cork. Thus the specimen tubes could be removed from the thermostat without disturbing the temperature equi-

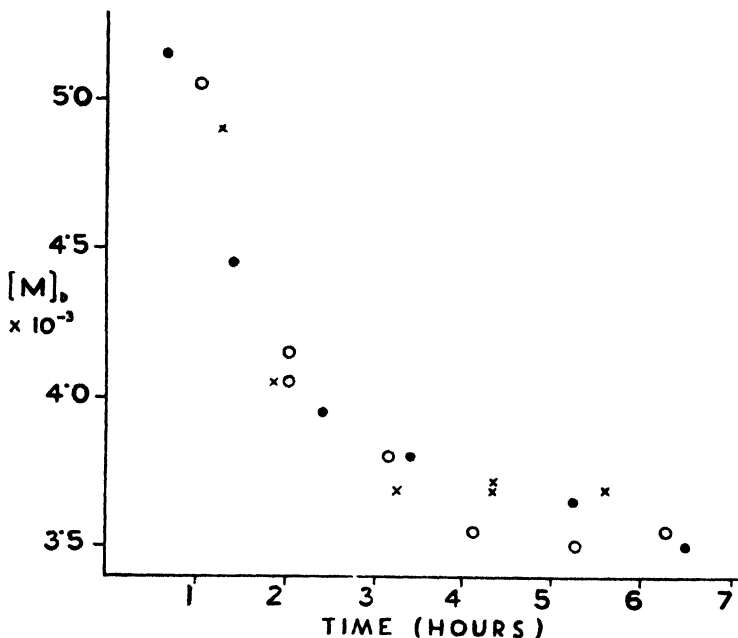


FIG. 5.

brium inside. At the beginning of an experiment the cruet was taken from the oven and a circular brass plate with a radial slit slipped underneath it to support the specimen tubes which were then inserted. Having adjusted the oven slightly above the required temperature the door was opened, the cruet set on the spindle, the plate withdrawn, and the door closed. Constant temperature was attained within five minutes of the commencement, but in any case several minutes must have elapsed before temperature equilibrium was completely established.

Two and sometimes three independent experiments were made at a given temperature, using both crystalline and powdered material. The results are too numerous to present in detail but in Fig. 5 are shown data obtained in three runs at 70°C . The dots and circles refer to crystals and powder, respectively, of the same preparation, and the crosses to a different preparation of crystals. In order to give an idea of the degree of reproducibility the points are plotted on a fairly large scale graph so that it has been necessary to omit some of the early measurements and all those later than seven hours after the start.

The $[M]_D$ values in Figs. 2 and 5 have been corrected for the negative contribution of strychnine ion. This amounts to about 0.25×10^3 degrees per mole of *tri*-strychnine salt and is therefore less than 4 per cent. of the rotatory power of the complexion.

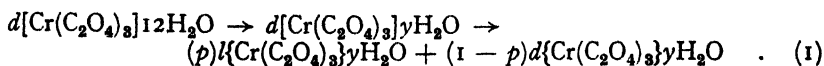
It should be noted in connection with Tables I and IV that in three out of four cases cited 0.04 gram was dissolved in 25 cc. of chloroform whereas in sample B of the *l* salt, 0.066 gram was used. The observation tube was 8 cms. in length.

Discussion.

There is abundant evidence that expulsion of water from the crystals is an essential first step in promoting racemisation. Phosphoric oxide *in vacuo* at room temperature completely removes the water in the space of five hours, during which time racemisation takes place to the extent of 10 per cent. and subsequently continues at a measurable rate for at least a fortnight. *The loss of rotatory power occurs, for the most part, after dehydration and not contemporaneously.* The independence of the two events though less obvious at elevated temperatures is almost certainly established, for under these circumstances the rate of racemisation in anhydrous material is greatly increased. This being the case, an accelerating initial phase would be anticipated though it is easy to see why it was never observed since on account of experimental limitations significant measurements cannot be made sooner than twenty minutes after the commencement of dehydration. By that time most of the water destined to be expelled at the working temperature will have been expelled and the reaction velocity will have attained a maximum value. The experiments are not sufficiently accurate to detect small irregularities in the rate-constant produced by subsequent loss of the last few per cent. of water.

A striking fact is the retention by the solid of between 10 and 20 per cent. of the original activity at high temperatures after the lapse of several days. On the whole it appears that the ultimate rotatory power is smaller the higher the temperature but this is not absolutely certain. Residual rotation is probably to be attributed to isolated domains within the crystals which for some reason remain essentially unchanged even though the water has gone. But in this connection there are a number of points to consider. Racemisation of a compound such as potassium *d*-chromioxalate *in aqueous solution* undoubtedly involves inversion of the molecular-ions; dextro-rotating configurations become lævo-rotating and vice versa. The time-averaged condition of all the complex ions is identical and the whole of the rotatory power eventually disappears when the solution contains equal numbers of the two enantiomorphs. On the other hand, the behaviour of a chromioxalate ion in a crystal lattice must be influenced to some extent by its position and the nature and whereabouts of its neighbours; small displacements and irregularities may have important consequences. When water is expelled, the intramolecular vibrations may take on larger amplitudes, but the removal of steric hindrance is only one of the factors involved in the racemisation process. It has been suggested (Part IV. of this series of papers) that water enters into the composition of the molecular-ions and when removed leaves them in an unstable "expanded" state. Because of certain constraints, individual chromioxalate ions may not "contract" immediately and when they do the chance of inversion is conceivably less than 0.5, *i.e.*, more than 50 per cent. of them contract without inversion.

With regard to the so-called constraints it should be noted that pulverising the P_2O_5 desiccated crystals in an agate mortar causes no immediate diminution of rotatory power. Indeed, it has been consistently observed that effects produced by powdering the crystals under various circumstances are either small or non-existent. The processes of dehydration and racemisation can perhaps be represented by the following scheme :



p (≈ 0.5) is the probability of inversion ; $\gamma = 0, 1, 2 \dots$, and p may vary with γ . The change from square to curly brackets represents "contraction." Partial loss of optical activity will occur without inversion ($p \rightarrow 0$) if the contracted state, or states, of chromioxalate ion possess smaller absolute rotatory power ; larger rotatory power is conceivable but theoretically unlikely. Without further elaborating these ideas it is apparent that the condition of the partially racemised solid is likely to be complex. Moreover, *all measurements of optical activity were made by dissolving the solid in chloroform* and the solvent may to some extent have the effect of rendering homogeneous the heterogeneous ensemble of molecular states assumed to exist in the crystals.

Information concerning the internal structure of the desiccated crystals is very desirable and may soon be forthcoming. The loss of all twelve molecules of water, at room temperature and at $120^\circ C$., takes place without noticeable effect on the appearance of the crystals except for a slight colour change, the dehydrated salt being distinctly greener. The greenness is an immediate result of dehydration and apparently unconnected with the occurrence of racemisation. No signs of disintegration are revealed by the microscope ; the outward form of the orthorhombic crystals is perfectly preserved and they remain lustrous and transparent. In polarised light straight extinction is given by both hydrated and dehydrated crystals. There is no reason, therefore, to suppose that a new crystal type with a racemic unit cell is built up during the solid phase reaction. For a racemate invariably possesses higher crystal symmetry than its optically active components. Five years ago the authors isolated a pseudo-racemate of *tri*-strychnine *cobalt*-oxalate, *i.e.*, l Str $_3$ $d[Co(C_2O_4)_3] \cdot 6H_2O$ which was hexagonal whereas the d and l salts are orthorhombic.* The large size and numerical preponderance of strychnine ions may control the characteristics of the lattice, so that the preservation of the original form during inversion of the chromioxalate ions is not altogether surprising.

The random occurrence of intramolecular rearrangement throughout the body of the pseudo-morph would, in the simplest case, conform to an exponential law. Further experimental work is necessary before it can be decided whether the partly exponential nature of the curves in Fig. 2 is fortuitous. The very fast initial phase of racemisation which figures so prominently at and above $70^\circ C$. is probably not connected with the rush of water from or through the crystals, although should equation 1 be reversible, the adsorption and desorption of water molecules by chromioxalate ions will provide them with numerous opportunities to assume opposite configurations. This may be a contributory factor. A relatively rapid loss of rotatory power during the first twenty-four

* The amount of crystal water in the racemate is not quite certain.

hours is also recorded at room temperature (Fig. 1), so there appears to be a mechanism of racemisation possessing a high temperature coefficient of velocity characteristic of the desiccated, or nearly desiccated, lattice. That the rate of racemisation in the dry solid is accelerated by rise of temperature has been proved by rapidly and completely dehydrating the crystals at room temperature and then transferring to an air-oven. This important result will be the starting point of future investigations.

The analyses of the heating-curves suggest that the exponential velocity constants of the so-called "fast phase" of racemisation are practically independent of temperature above 70° C., but until further experiments have been made it seems unprofitable to discuss the matter. At 60° and 48° C., the slower exponential rates may be partly ascribed to the retention by the crystals of significant amounts of water during the "fast phase" of racemisation and partly to a genuine temperature coefficient of velocity. The rate at room temperature is only six times slower than at 48°, but in this case the reaction takes place in a water-free medium. The question as to what extent, if any, the probability factor p depends on water-content and temperature must be left open for the present. It is interesting to note that the ultimate amounts of racemisation at room temperature (P_2O_5) and at 100° C. are approximately equal.

The general considerations outlined above account very well for the anomalous behaviour of *tri*-strychnine *l* chromioxalate. The spontaneous evaporation of chloroform of crystallisation leaves the pseudomorph in a condition to undergo partial racemisation at room temperature. The smaller diminution of rotatory power under all conditions signifies either that crystallisation from chloroform results in a greater proportion of molecular-ions in a "collapsed" state and hence unable (or less able) to suffer racemisation, or that the probability factor p is correspondingly small. The extent to which the 5 per cent. of water present controls the course of racemisation will depend on the age of the material. Our observations definitely dispose of the idea that the last few per cent. of water are especially active in promoting the change.

The peculiar curves of dehydration shown in Fig. 2 are worthy of attention. After the initial rapid loss of water, the rate slows down practically to zero and the substance can be kept at any particular temperature for many hours, and even days, without significant change in weight. The release of water molecules from equilibrium positions in the crystal lattice will be governed by quantities of the type $Ke^{-\phi/kT}$, ϕ being a work function of variable magnitude. If, as the results seem to imply, the desiccated lattice does not collapse, the deeper potential minima vacated by molecules in the surface layers of the crystallites will trap others arriving from the interior. Therefore, the chance that a water molecule will escape from the crystal (as distinct from the lattice points) diminishes rapidly with its initial distance from the surface and with the degree of desiccation but increases with rise of temperature. Hence, the dehydration curves flatten out at progressively higher levels. We appear to be dealing with an adsorption phenomenon similar in some respects to that met with in the zeolites,³ for although the crystals normally contain twelve molecules of water, the process of dehydration cannot be said to give rise to definite lower hydrates. The desiccated

³ Rothmund, *Rec. Trav. Chim.*, 1925, 44, 329; Tiselius, *Z. physik. Chem.*, 1934, 169A, 425.

crystals readily absorb moisture from the atmosphere and under favourable circumstances almost regain their original weight. It is interesting to note that at 48° C., whereas only three quarters of the water is expelled, the loss of rotatory power amounts to nearly 35 per cent. in twenty-four hours.

In conclusion, it may be remarked that racemisation in the crystalline state of other co-ordination compounds are at present under investigation in this laboratory, and we are inclined to think it will be possible to establish some general principles underlying solid reactions of this type.

Summary.

A start has been made on the quantitative investigation of racemisation of co-ordination compounds in the crystalline state. The behaviour of the *tri*-strychnine salts of *d* and *l* chromioxalate has been studied at various temperatures and tentative conclusions drawn regarding the mechanism of intramolecular rearrangement. Incidentally, it is believed that both enantiomorphs have been prepared for the first time in a condition of almost perfect optical purity.

One of us (C. H. J.) wishes to thank the Colston Society of Bristol for grants in aid of this research, and the other (A. M.) is indebted to the Department of Scientific and Industrial Research for a maintenance grant.

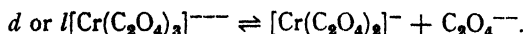
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PART VI.—RACEMISATION OF POTASSIUM CHROMIOXALATE IN AQUEOUS SOLUTION. THE ACCELERATING INFLUENCE OF IONS.

BY N. W. D. BEESE AND C. H. JOHNSON.

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Up to the present no really comprehensive study of the manner of racemisation of any co-ordination compound has been undertaken. Indeed, the only contribution to the subject is a paper by Rideal and Thomas¹ who determined approximate values of the unimolecular velocity constants for potassium chromioxalate at four temperatures between 0° and 24° C. A theory of racemisation proposed by Thomas² assumes the following equilibrium to be set up when the salt is dissolved in water:



The dissociation is attended by loss of activity since re-orientation of the two remaining oxalate radicles occurs, and in the reverse process there is an equal probability of formation of either optical isomer.

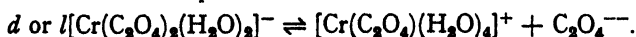
Now this theory disregards the solvent, whereas if two molecules of water enter the vacant co-ordination positions they might in turn be replaced by oxalate without inversion of the original configuration.

¹ *J.C.S.*, 1922, 121, 196.

² *J.C.S.*, 1921, 119, 1140.

Re-examination of Werner's so-called *cis*³ and *trans*⁴ diaquo-dioxalato salts of chromium has revealed an unexpected anomaly. Consequently we would not care to make any statement, at present, regarding the possible participation of these ions in the racemisation process. It is quite certain, however, that if oxalate ions become detached they rapidly re-unite, for it is impossible to detect their presence in solution⁵ and the absorption coefficients remain unchanged during racemisation.

Carrying the ionisation a stage further and including solvent molecules for the sake of completeness:—



This second step must inevitably be accompanied by loss of activity because the complex cation is not dissymmetric. In the absence of precise information the two stage process of ionisation seems a more logical postulate than that of Thomas, since taking place rather infrequently owing to the excessively small concentration of the ion on the left-hand side of the equation it would account for the slow rate of racemisation; slow, that is to say, by comparison with ionic reactions generally. A little consideration shows that either ionisation mechanism, particularly the second, is likely to be retarded by addition of a soluble oxalate to the solution, and to some extent by increasing the concentration of chromioxalate. Both these conditions have been examined but before presenting the results it is desirable to describe the experimental technique.

Experimental.

Rideal and Thomas¹ kept a large quantity of potassium chromioxalate in a thermostat from which amounts were withdrawn periodically and quickly examined in a polarimeter tube maintained at the same temperature. As the time of half change is only about 30 minutes at 18° C. the method has obvious objections, and it is common experience that small temperature fluctuations inside a polarimeter tube distort the image. We have therefore adopted a different plan.

A thermostat was set up close beside the polarimeter regulated to $\pm 0.01^\circ$ and stirred by a fan attached to an Archimedian screw which circulated the water to a smaller thermostat, well lagged, mounted between polariser and analyser. It was found easily possible to keep the temperature in the small thermostat constant to $\pm 0.02^\circ$ C. during the course

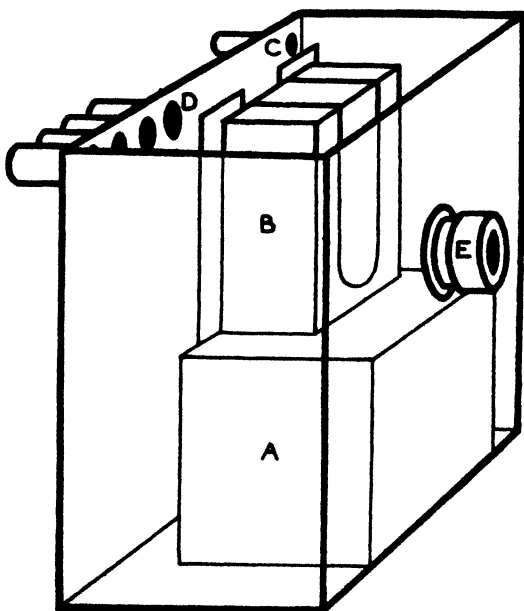


FIG. 1.

³ Werner, *Ann. Chem.*, 1914, 406, 261.

⁴ Croft, *Phil. Mag.*, 1842, 21, 197.

⁵ Johnson, Part IV. *This vol.*, p. 1612.

of an experiment. The arrangement is shown in Fig. 1. A heavy brass block, A, supporting a rectangular glass cell, B, was fitted with upright strips to which the cell was lightly clamped by means of a rubber band. The inflow pipe is marked, C, and the wider outflow pipes, D, leading back to the main thermostat, but two sensitive thermometers placed at C and D are not shown in the diagram, neither is the lid (lagged with felt) which covered the thermostat when in use. In addition to the thermometers, the spindle of a stirrer also passed through the lid. No oil or grease could be used on the bearings for these when dispersed in water caused blurring of the field of observation. Both thermostats, therefore, had to be kept scrupulously clean. The screw caps, E, only one of which can be seen in the figure, were provided with ample rubber washers so that water-tightness was achieved without strain on the glass windows. The cell, B, consisted of two strain-free, optically worked glass plates separated by a U-shaped piece accurately ground on the parallel faces. Three such cells of thicknesses 19, 2, and 0.5 mm. were made for us by Messrs. Bellingham & Stanley Ltd. A smear of vaseline rendered the cell water-tight and rubber bands were placed around top and bottom as an additional precaution.

Having mounted the cell and adjusted the temperature, a weighed quantity, 0.045 gr., of $K_2dCr(C_2O_4)_2 \cdot 2H_2O$ was added to a weighed amount, 10 grams, of distilled water at the working temperature. The solution was at once transferred to the cell, by pipette or pouring as convenient, the whole operation occupying about a minute. Investigation showed that the temperature of the solution immediately after making up differed from the thermostat by less than 0.2° and that thermal equilibrium was completely established within five minutes of introducing it into the cell. For a minute or two after filling the field was a trifle indistinct but soon settled down and thereafter *continuous observations of rotatory power could be made under isothermal conditions*. The source of illumination was a sodium vapour lamp but the observer sat in a dark cubicle.

Zero readings taken through the cell containing a racemic solution of potassium chromioxalate were not appreciably different from those recorded with the cell removed. Using a half-shadow angle of 5° settings were reproducible to 0.01° . Freshly resolved potassium *d* chromioxalate⁶ gave initial rotations of about 0.9° . Unless otherwise stated the dextro-rotatory salt was invariably used; its preparation is described in Parts IV. and V. of this series. The working temperature has been $18.2 \pm 0.02^\circ C$. throughout.

The plot of $\log_{10} \frac{R_0}{R_t}$ against the time is linear, R_0 being the initial rotation and R_t the rotation after time, t . The two optical isomers are undergoing rapid inter-conversion in solution so we may write:—

$$\frac{dx}{dt} = k(a - 2x),$$

a being the initial concentration of, say, d chromioxalate ions and x the concentration of l chromioxalate after a lapse of time t . k is the velocity constant of inversion. Whence:

$$\begin{aligned} k &= \frac{1}{2t} \ln \frac{a}{(a - 2x)} \\ &= \frac{2.303}{2t} \log_{10} \frac{R_0}{R_t} \end{aligned}$$

The unimolecular velocity constants have thus been computed from pairs of polarimeter readings. Averaged values of k will be found in the Tables which follow. Occasionally there has been an indication that the rate increased abruptly, though slightly, about half-way through the run. We have therefore examined statistically the results of ninety-two experiments made under a variety of conditions as regards concentration of

chromioxalate or added salt, by comparison of k' calculated from the first five trustworthy observations with k the velocity constant averaged from all significant readings.

$k > k'$	in 12 experiments
$k > k'$	50 "
$k = k'$	1 "
$k < k'$	29 "
$k < k'$	0 "

$k > k'$ means a difference of from five to fifteen per cent. We are unable to offer an explanation as there is no regularity whatever in the conditions under which relatively large positive deviations have been recorded. Lack of temperature control is not the cause.

Effect of Concentration and Addition of Common Ions.

By employing a metal water-jacketed tube of length 205 mm. and the three glass cells previously mentioned the rate of racemisation of $K_2dCr(C_2O_4)_2$ in pure water was measured at concentrations between 6.4×10^{-4} molar (0.03 per cent.) and 6.0×10^{-1} molar (28 per cent.), i.e., a thousandfold variation. Two or three determinations were made at each concentration, and the results were quite concordant (Table I.).

TABLE I.

Concentration Mols./Litre.	$k \times 10^3$.
0.00064	0.180
0.0096	0.176
0.0875	0.195
0.32	0.225
0.60	0.247

TABLE II.

Concentration of $K_2dCr(C_2O_4)_2$ (Mols./Litre).	Concentration of $K_2C_2O_4$ (Mols./Litre).	$k \times 10^3$.
0.0096	0	0.173
0.0096	0.066	0.192
0.0096	0.50	0.257
0.0096	1.5	0.390

At the three lowest concentrations the values of k are barely distinguishable but the other two show an upward trend with increasing concentration. One experiment was carried out at 0.0096 M in the 19 mm. cell packed with glass wool; the observed rate constant, $k = 0.191 \times 10^{-3}$, indicates that the racemisation process is not significantly catalysed by a glass surface. The *levo* salt, $K_2lCr(C_2O_4)_2$, gave $k = 0.171 \times 10^{-3}$ at a concentration of 0.0096 M .

Experiments with aqueous potassium oxalate ("common ions") as solvent are summarised in Table II.

Thus, far from reducing the rate of racemisation, increased concentration and addition of common ions actually augment it. This result definitely rules out the two-stage ionisation mechanism of racemisation. Since calcium chloride, 1*M*, fails to produce a precipitate of calcium oxalate when added to potassium *d* chromioxalate it is clear that the concentration of free oxalate ions is increased by a factor of at least 10^3 when the compound is dissolved in fairly concentrated solutions of potassium oxalate; yet the loss of rotatory power is not retarded. Therefore as regards the one-stage hypothesis of Thomas, either the time between dissociation and re-arrangement is small compared to the interval between fruitful collisions with oxalate even in the presence of an overwhelming quantity of potassium oxalate, in which case the velocity of racemisation is equal to the velocity of ionisation,* or as seems equally probable to us, racemisation does not involve dissociation but is an intramolecular re-arrangement with participation

* Cf. Bergmann and Polanyi, *Naturwiss.*, 1933, 21, 378.

of solvent. When potassium oxalate enriched in the heavier isotopes of oxygen can be prepared it will be possible to settle this question.

Addition of Foreign Ions.

The accelerating influence of many salts * upon the rate of racemisation was first brought to our notice by unsuccessful attempts to obtain optically active chromioxalates, other than those of the alkali metals, from *tri* strychnine *d* chromioxalate.

From this point onwards, all experiments were made with



at a concentration of 0.0096 *M* in the 19 mm. cell. The salt solution under investigation was prepared by dissolving a weighed amount in 10 grams of water in a small stoppered flask. This was suspended in the main thermostat and having attained the working temperature, $18.2 \pm 0.2^\circ C.$, was used as solvent for the chromioxalate in the manner already described.

(a) **Monovalent Cations** (Table III.).—It is evident that quite large concentrations ($> 0.05 M$) of most univalent cations are required in order appreciably to increase the speed of racemisation; also that the effect produced by anions is insignificant with the exception of OH^- . When

TABLE III.

(Monovalent Anions.)			(H ⁺ , OH ⁻ and Polyvalent Anions).		
Compound.	Concentration (Mols./Litre).	$k \times 10^3$.	Compound.	Concentration (Mols./Litre).	$k \times 10^3$.
—	0	0.173	HCl	0.001	0.180
LiCl	0.50	0.244	"	0.0025	0.195
"	4.2	1.24	"	0.01	0.208
KCl	0.50	0.213	"	0.08	2.47
NH ₄ NO ₃	4.2	0.366	HNO ₃	1.0	2.56
"	7.1	0.382	NaOH	1.0	0.585
"	10.0	0.359	KOH	0.54	0.484
AgNO ₃	0.00056	0.177	K ₂ SO ₄ (NH ₄) ₂ SO ₄ " " K ₄ Fe(CN) ₆	0.50	0.240
"	0.10	0.382		0.50	0.272
"	0.20	0.551		1.5	0.416
"	0.50	0.953		3.8	0.795
TiNO ₃	0.10	0.360		0.50	0.275
Hg ₂ (NO ₃) ₂	0.005	1.78			

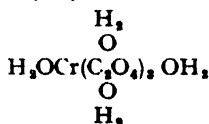
comparing the behaviour of, say, KCl with that of K₂SO₄ and K₂C₂O₄ at the same molality it must be borne in mind that although more or less equivalent as regards anions, the concentration of K⁺ is approximately doubled in the solutions of sulphate and oxalate, so their accelerating influence which is also about twice that of KCl can be confidently attributed to cation catalysis. In this connection it is noteworthy that K₂SO₄

* It must be emphasised in connection with experiments involving the addition of salts to solutions of potassium chromioxalate that in practically all cases recorded in the Tables, at the specified concentrations, the solutions remained unchanged apart from loss of rotatory power during the time of observation and, generally speaking, for many hours afterwards. We shall shortly communicate a paper dealing with a spectroscopic investigation of the destruction of chromioxalate by polyvalent cations, but even in the presence of trivalent cations the time taken for appreciable decomposition to occur is long in comparison with that required for complete racemisation. Reference should also be made to Part IV.

and $(\text{NH}_4)_2\text{SO}_4$ produce accelerations quantitatively akin to $\text{K}_2\text{C}_2\text{O}_4$ ("common ions") and that the self-catalytic effect observed on increasing the concentration of potassium chromioxalate is of the same order of magnitude. Since chromioxalate ion carries three negative charges it will strongly repel anions in proportion to the product of the charge on each; thus the relative impotence of anions is scarcely surprising.

Acceleration by H^+ is appreciable at concentrations greater than 0.002 N . Li^+ exerts a more powerful influence than the other alkali metals, and Ag^+ and Tl^+ are quite outstanding in this respect. The latter, being eighteen electron-shell ions, give rise to a variety of physical properties conventionally though vaguely ascribed to "deformation" which may also be invoked here. The case of mercurous ion, Hg_2^{2+} is particularly interesting. As will be seen from the next section, it behaves similarly to *divalent* ions of transitional metals. In order to minimise hydrolysis the salt was dissolved in 0.01 N HNO_3 for the catalytic effect of H^+ at this concentration is slight. Comparison of the catalytic activities of Ag^+ , Tl^+ and Hg_2^{2+} proves that the concentration of Tl_2^{2+} in 0.1 M TlNO_3 is exceedingly small.⁷ The acceleration produced by Ni^{2+} is about equal to that of Hg_2^{2+} ; therefore an experiment was carried out with 0.01 M $\text{Ni}(\text{NO}_3)_2$ in 0.01 N HNO_3 , the identical acid used in making up the solution of mercurous nitrate. The rate was scarcely affected by the presence of H^+ , showing that the latter does not induce abnormal behaviour in other ions.

The acceleration produced by OH^- is surprising even though its "volume" in crystals is only about half that of Cl^- , for it will be strongly repelled by chromioxalate ion. That it decomposes the complex is evident from the colour change which occurs after a few minutes in 1 M NaOH . On the other hand, Ca^{2+} at the same concentration although exerting a more pronounced catalytic effect upon the rate of racemisation causes no measurable decomposition during the time required for complete loss of rotatory power. How then does OH^- manage to disrupt the complex ion which it cannot closely approach? It has previously been suggested that water must be included in the composition of *tri*-oxalate ions,⁶ which although loosely bound gives rise to important results. Let us represent the situation diagrammatically by:



The number of water molecules chosen is purely arbitrary. On the approach of hydroxyl ions the protons on the water molecules will find it difficult to decide to which oxygen nucleus they belong and there will be a high probability of complete transference to nearby OH^- ions. When this happens one or more hydroxyl radicals will be left in the immediate vicinity of chromioxalate and reaction can occur.

Experiments were carried out with ammonium nitrate at high concentrations in order to discover the effect of largely replacing water molecules in the solvent by solvated ions and ion-pairs. The rate of racemisation reaches a maximum in the neighbourhood of 7 M . Similar experiments with the very soluble salts LiCl and KNO_3 failed; potassium chromioxalate would not dissolve in LiCl aq. at concentrations greater than 5 M and the other gave cloudy solutions.

(b) **Divalent Cations** (Table IV.).—Broadly speaking, divalent cations increase the speed of racemisation to the same extent as monovalent at one hundredth the concentration. But wide variation in effectiveness is manifest within the divalent class. The alkaline earths are feeble by comparison with ions of transitional metals. It is not clear why Ca^{2+} should occupy such a prominent position amongst the members of Group

⁷ Cf. Drücker, *Z. Elektrochem.*, 1922, 28, 463.

II, but the inferiority of Be^{2+} may be partly due to its permanent state of hydration as $\text{Be}(\text{H}_2\text{O})_6^{2+}$ and partly to complex formation with sulphate

TABLE IV.

Compound.	Concentration Mols./Litre.	$k \times 10^3$.
—	0	0.176
BeSO_4	0.01	0.211
MgCl_2	0.01	0.263
CaCl_2	0.0112	0.468
$\text{Sr}(\text{NO}_3)_2$	0.01	0.275
BaCl_2	0.01	0.298
MnCl_2	0.0107	0.421
$\text{Co}(\text{NO}_3)_2$	0.01	0.726
$\text{Ni}(\text{NO}_3)_2$	0.01	1.58
CuSO_4	0.01	2.49
ZnSO_4	0.01	1.18
CdSO_4	0.01	0.440
HgCl_2	0.01	0.179
$\text{Zn}(\text{en})_2\text{SO}_4$	0.01	0.525
$\text{Zn}(\text{en})_2\text{Cl}_2$	0.01	0.550

ions. Mn^{2+} resembles Ca^{2+} and each has an S ground state. As previously remarked, there is a rough parallelism between catalytic activity and "deforming" character as observed in the crystalline halides. Both attain a maximum in Cu^{2+} . Mercuric chloride shows itself to be a weak electrolyte, for it does not augment the rate.

The cases of $\frac{1}{2}$ ethylenediamine zinc sulphate and chloride are included in order to illustrate the application of this technique to the study of co-ordination compounds. Their pronounced catalytic activity rather suggests that

the complex ion is considerably broken down in solution. Neozi and Mukherjee⁸ however claim to have resolved it into optical isomers.

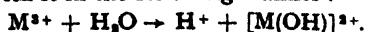
(c) **Trivalent Cations** (Table V).—Trivalent ions are sharply differentiated by these experiments into two groups. La^{3+} and Ce^{3+} can in a sense be regarded as "normal" because far less susceptible to external influences than ions of transitional metals on account of their unique electron configurations. This aloofness, so characteristic of the rare earth ions, is reflected in magnetic and spectroscopic properties. The difference in catalytic activity between them and an average alkaline earth metal is almost as marked as between the latter and an alkali metal.

On the other hand, aluminium and chromium, and probably ferric ion too, resemble the feeble sort of divalent ions. Association with anions is unlikely to be the

TABLE V.

Compound.	Concentration (Mols./Litre).	$k \times 10^3$.
$\text{La}(\text{NO}_3)_3$	0.001	0.719
"	0.0001	0.222
$\text{Ce}(\text{NO}_3)_3$	0.001	0.811
"	0.0001	0.231
$\text{KAl}(\text{SO}_4)_3 \cdot 12\text{H}_2\text{O}$	0.01	0.297
"	0.001	0.194
"	0.001 (H_2SO_4 , 10^{-2}N)	0.203
$\text{Cr}(\text{NO}_3)_3$	0.01	0.341
"	0.001	0.205
$\text{KCr}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$	0.001	0.192
$\text{KFe}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$	0.001 (H_2SO_4 , 0.05N)	0.389

explanation since the nitrates are not appreciably different from the alums, neither is the postulate of an excessive edgree of hydration at all convincing. We tentatively suggest that these trivalent ions are unstable in water and react with it in the following manner:



Doubtless the conditions are complex but perhaps the ion $[\text{M}(\text{OH})]^{2+}$ is present in relative abundance.

Attempts to study the effects of co-ordination by introducing $[\text{Co}(\text{NH}_3)_6]^{3+}$, $[\text{Co}(\text{en})_3]^{3+}$ and the corresponding complex ions of Cr^{3+}

TABLE VI.

Solution Data.		Rate Constants.	
Concentration (Mols./Litre).	Activity Coefficients γ .	$k \times 10^3$.	Mean $k \times 10^3$.
CaCl_2			
0.2208	0.478	1.83	1.84
0.2208	0.478	1.85	
0.1830	0.484	1.63	1.65
0.1830	0.484	1.67	
0.1479	0.495	1.49	1.54
0.1479	0.495	1.59	
0.1119	0.509	1.28	1.31
0.1119	0.509	1.35	
0.0824	0.525	1.10	1.17
0.0824	0.525	1.23	
0.0556	0.560	0.992	0.981
0.0556	0.560	0.969	
0.0446	0.581	0.836	0.900
0.0446	0.581	0.964	
0.0301	0.621	0.757	0.773
0.0301	0.621	0.790	
0.0271	0.631	0.697	0.691
0.0271	0.631	0.685	
0.0112	0.715	0.470	0.468
0.0112	0.715	0.466	
0.00455	0.792	0.322	0.323
0.00455	0.792	0.323	
0.00275	0.830	0.263	0.264
0.00275	0.830	0.264	
0.00165	0.860	0.230	0.233
0.00165	0.860	0.237	
0.00083	0.896	0.209	0.210
0.00083	0.896	0.211	
0	—	—	0.176
MnCl_2			
0.4033	0.480		1.88
0.2013	0.501		1.33
0.1005	0.543		1.02
0.0505	0.594		0.717
0.0307	0.638		0.589
0.0203	0.671		0.500
0.0107	0.731		0.421
0.0053	0.790		0.308
0	—		0.179
CuCl_2			
0.00514	0.788		1.61
0.00417	0.804		1.33
0.00344	0.821		1.14
0.00209	0.852		0.755
0.00104	0.892		0.454
0	—		0.188
0	—		0.186

Dependence of the Rate of Racemisation upon Concentration of Added Salt.

It was decided to investigate quantitatively the catalytic action of calcium chloride, manganese chloride and cupric chloride. Ca^{2+} has a rare-gas-like structure; Mn^{2+} is a symmetrical ion and Cu^{2+} the most potent divalent cation. The salts were "Analytical

Reagents" supplied by British Drug Houses Ltd. They were analysed

qualitatively and found to be absolutely pure within the specifications; the minute traces of impurities were unimportant. Solutions were prepared with distilled water in calibrated flasks and the concentrations checked by volumetric analysis. Two measurements of the rate of racemisation were made at each concentration, the chromioxalate being, as usual, 0.0096*M* and the temperature $18.2 \pm 0.02^\circ \text{C}$. Complete data for CaCl_2 , aq are given in Table VI. in order that an estimate may be formed of the reproducibility of the velocity constants. Averaged values of k are listed for the other

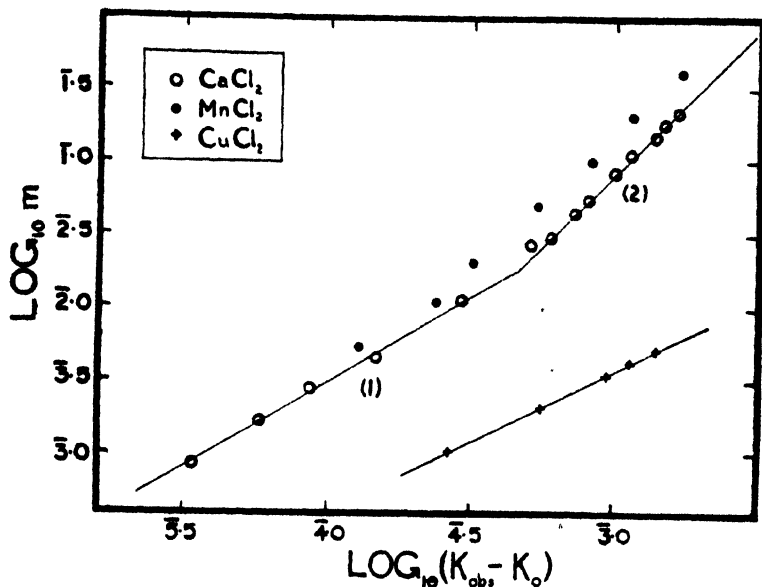


FIG. 2.

two compounds. Practical considerations severely limit the range of concentration of the salt solutions. It is impossible to make visual observations with accuracy when the time of half-change is less than three minutes, and at great dilution the values of $(k_{\text{obs}} - k_0)$ become comparable with the uncertainties in k_0 . The simplest likely relationship between velocity constant and concentration of salt can be expressed as follows:

$$k_{\text{obs}} = k_0 + A(m)^n$$

k_{obs} and k_0 refer to concentrations m and zero respectively. Since in fact k_{obs} is, at most, ten times larger than k_0 , the latter cannot be disregarded, although employment of the uncatalysed rate constant when m is large is open to question. In Fig. 2, $\log_{10} (k_{\text{obs}} - k_0)$ is plotted against $\log m$.

TABLE VII.

Ion.	n .	
	(m).	(α) \pm .
$\text{Ca}^{2+}, \text{Mn}^{2+}$	(1) .87	.89
	(2) .50	.58
Cu^{2+}	1.04	1.13

derived from data given by Landolt-Börnstein (*Physikalisch-Chemische Tabellen*, 1931, p. 1114 *et seq.*), and the ion-activities, α \pm , calculated by

means of Lewis and Randall's formula (*Thermodynamics*, p. 328) which reduces to $\alpha \pm = 1.587 \gamma m$ in the case of MCl_2 , γ being the activity coefficient. The graphs of $\log (k_{obs} - k_s)$ against $\log \alpha \pm$ were similar in all respects to those in Fig. 2. Values of n (previous equation) were obtained from the slopes of the lines given in Table VII.

It is not clear why the exponent n should change abruptly from about 1 to about 0.5 on increasing the concentration of the salt. It appears, however, that the racemising action of Cu^{2+} is simpler than for the other two ions in spite of its more pronounced influence, which may be due to predominance of the mechanism requiring $n = 1$ within this range of concentration. Another peculiar and unexplained result is the linear relationship between $\log k_{obs}$ and $\log \gamma$ depicted in Fig. 3.

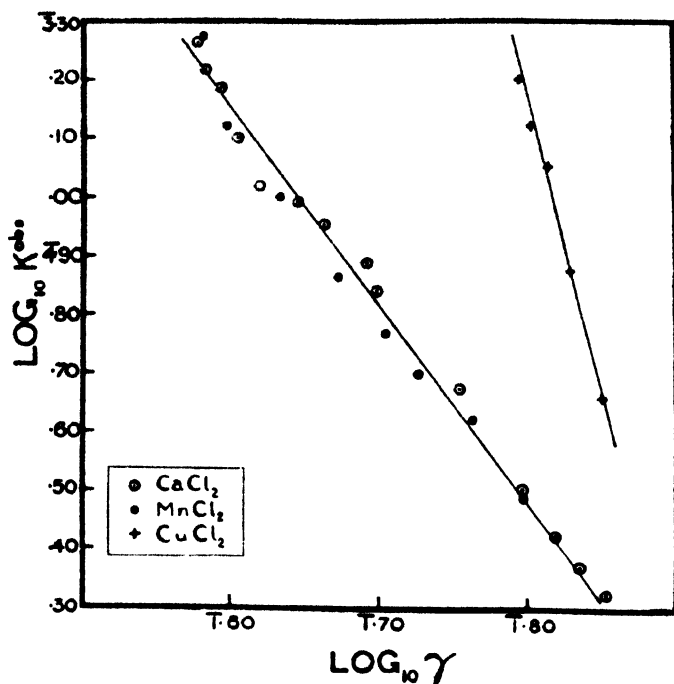


FIG. 3.

Much remains to be done in the quantitative examination of these interesting cases of cation catalysis. We are also extending our observations to the monovalent complex ions



Summary.

The inability of oxalate ion to depress the rate of racemisation of potassium chromioxalate when present in solution at high concentration admits of two alternative explanations. Either racemisation is a measure of the rate of ionisation, or else racemisation does not involve ionisation.

The loss of optical activity is markedly accelerated by positive ions, the effect increasing with the valence number. This promises to be a very useful indicator reaction since it appears to give reliable information concerning the cations in solution. Thus Ag^+ and Tl^+ exhibit greater catalytic activity than the alkali metals but are feeble in comparison with

divalent ions. Judged by its accelerating influence mercurous ion is a doubly charged unit, Hg_2^{2+} . On the other hand, the weak electrolyte mercuric chloride is totally inert. We have so far obtained no indication of the existence of Ti_3^{3+} nor of Cr^{3+} or Al^{3+} , which behave in water as though constituted $[\text{Cr}(\text{OH})]^{3+}$ and $[\text{Al}(\text{OH})]^{3+}$ respectively. It is hoped to apply this method to the examination of complex ions in solution, particularly those of moderate stability, with a view to determining the extent of dissociation.

The catalytic activities of three pure salts, CaCl_2 , MnCl_2 , and CuCl_2 , have been studied over a wide range of concentration.

We are very greatly indebted to the Department of Agriculture for the loan of a polarimeter without which the work could not have been commenced, and to the Colston Society of Bristol for the purchase of special glass cells used in the research.

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THE SURFACE TENSIONS OF BINARY LIQUID MIXTURES CONTAINING BENZENE.

By J. W. BELTON.

Received 1st October, 1935.

The calculation of the adsorption at the surface of a binary liquid mixture requires a knowledge of the variation of the surface tension and of the activities of the components with composition. In the case of mixtures of organic liquids, the former necessitates a high degree of accuracy in the surface tension measurements, for the surface tensions of the pure components are not usually widely separated, while the latter may be obtained from their partial vapour pressures. The mixtures described below, in each of which one component is benzene, were chosen for investigation because their partial vapour pressures are known and because they each give a very different form of adsorption-composition curve.

Experimental.

The surface tensions were measured by the bubble pressure method previously described by the writer.¹ The surface tensions were calculated from the relation

$$\gamma = \frac{rg}{2}(h\rho - \frac{2}{3}r\rho_1),$$

where r is the radius of the jet (0.0102 cm.), g is 981.2 cm./sec.², h is the maximum bubble pressure in centimetres of butyl phthalate, the manometric liquid, ρ is the density of butyl phthalate at the temperature of the determination, and ρ_1 is the density of the liquid examined. The values obtained for the surface tensions of pure water and of pure benzene were in good agreement with the accepted values and with values obtained for both liquids by the capillary rise method. The chemicals used were of analar grade and were further purified until they gave a boiling-point or freezing-point and a surface tension of the accepted values.

¹ Belton, this vol., 1413 and 1420.

TABLE I.

Mixture.		λ .		γ .	
Benzene Plus.	Moles Per Cent. Benzene.	20°.	35°.	20°.	35°.
(a) Acetic acid.	0	5.24	5.01	27.42	25.99
	13.81	5.15	4.895	26.95	25.40
	30.85	5.14	4.86	26.90	25.21
	40.34	5.165	4.88	27.02	25.32
	50.47	5.20	4.90	27.21	25.43
	74.15	5.31	5.01	27.79	25.99
	100.00	5.52	5.185	28.89	26.91
		20°	30°	20°	30°
(b) Carbon disulphide	0	6.185	5.94	32.38	30.91
	7.89	5.93	5.705	31.04	29.69
	16.84	5.77	5.54	30.20	28.82
	28.23	5.65	5.45	29.56	28.36
	46.74	5.55	5.335	29.04	27.75
	63.81	5.53	5.295	28.94	27.55
	100.00	5.52	5.29	28.89	27.52
		50°		50°	
(c) Carbon tetrachloride	0	4.48		22.98	
	20.19	4.525		23.21	
	35.32	4.575		23.47	
	52.88	4.635		23.78	
	67.85	4.695		24.09	
	81.85	4.755		24.39	
	100.00	4.87		24.98	

TABLE II.—BENZENE—ACETIC ACID MIXTURES.

Moles Per Cent. C_6H_6 .	γ .	$\Delta\gamma$.	$p_{C_6H_6}$.	p_{HAc} .	$\Delta \log p$.	$\Gamma \times 10^{10}$.
20°						
0	27.42		0			
		0.20				
5	27.22		10			
		0.18			0.28	0.11
10	27.04		19			
		0.16			0.27	0.10
20	26.88		35.5			
30	26.89			7.6		
		0.09			0.068	0.23
40	26.98			6.5		
		0.14			0.089	0.27
50	27.12			5.3		
		0.24			0.101	0.42
60	27.36			4.2		
		0.30			0.118	0.45
70	27.66			3.2		
		0.34			0.183	0.33
80	28.00			2.1		
		0.43			0.243	0.32
90	28.43			1.2		
		0.46				
100	28.89			0		

TABLE II.—BENZENE—ACETIC ACID MIXTURES.—*Continued.*

Moles Per Cent. C_6H_6 .	γ .	$\Delta\gamma$.	$p_{C_6H_6}$.	p_{HAC} .	$\Delta \log p$.	$\Gamma \times 10^{10}$.
35°						
0	25.99		0			
		0.28				
5	25.71		18			
		0.20			0.408	0.09
10	25.51		46			
		0.22			0.176	0.21
20	25.29		69			
		0.08			0.096	0.14
30	25.21		86			
40	25.23			14.8		
		0.11			0.073	0.26
50	25.34			12.5		
		0.22			0.084	0.44
60	25.56			10.3		
		0.28			0.104	0.46
70	24.84			8.1		
		0.33			0.131	0.43
80	26.17			6.0		
		0.36			0.176	0.35
90	26.53			4.0		
		0.38				
100	26.91			0		

The following mixtures were examined between 0-100 per cent.: (a) benzene and acetic acid at 20° and 35°; (b) benzene and carbon disulphide at 20° and 30°; (c) benzene and carbon tetrachloride at 50°. The mixtures were made up by weight and were kept in stoppered bottles.

TABLE III.—BENZENE—CARBON DISULPHIDE MIXTURES.

Moles. Per Cent. C_6H_6 .	γ .	$\Delta\gamma$.	p .	$\Delta \log p$.	$\Gamma \times 10^{10}$.
20°					
0	32.38		0		
		1.58			
10	30.80		11.7		
		0.80		0.258	0.55
20	30.00		21.2		
		0.50		0.136	0.66
30	29.50		29.0		
		0.32		0.089	0.64
40	29.18		35.6		
		0.18		0.075	0.43
50	29.00		42.3		
		0.06		0.062	0.17
60	28.94		48.8		
		0.02		0.058	0.06
70	28.92		55.7		
		0.01		0.053	0.03
80	28.91		62.9		
		0.01		0.043	0.04
90	28.90		69.5		
		0.01		0.034	0.05
100	28.89		75.2		

TABLE III.—BENZENE—CARBON DISULPHIDE MIXTURES.—*Continued.*

Moles Per Cent. C_6H_6 .	γ .	$\Delta\gamma$.	p .	$\Delta \log p$.	$\Gamma \times 10^{10}$.
30°					
0	30.91		0		
		1.49			
10	29.42	0.74	17.4	0.265	0.48
20	28.68	0.42	32.0	0.143	0.51
30	28.26	0.34	44.5	0.100	0.59
40	27.92	0.24	56.0	0.072	0.57
50	27.68	0.10	66.1	0.063	0.27
60	27.55	0.04	76.4	0.057	0.12
70	27.54	0.01	87.0	0.051	0.03
80	27.53	0.01	98.0	0.047	
90	27.52	0	109.2	0.039	0.02
100	27.52		119.3		

TABLE IV.—BENZENE—CARBON TETRACHLORIDE MIXTURE.

Moles Per Cent. C_6H_6 .	γ .	$\Delta\gamma$.	p .	$\Delta \log p$.	$\Gamma \times 10^{10}$.
50°					
0	22.98		308		
		0.13		0.045	0.47
10	23.11	0.13	275	0.049	0.43
20	23.24	0.14	248.5	0.056	0.40
30	23.38	0.17	218.5	0.065	0.42
40	23.55	0.18	188	0.073	0.40
50	23.73	0.20	159	0.086	0.38
60	23.93	0.21	130.5	0.126	0.27
70	24.14	0.20	97.5	0.169	0.19
80	24.34	0.31	66	0.288	0.17
90	24.65	0.33	34		
100	24.98		0		

The surface tensions obtained were plotted against the composition of the mixture (in moles per cent.) and in all cases smooth curves resulted, the variation being within 0.04 dyne/cm.; these experimentally determined values are given in Table I. From the curves the surface tension was read off for every 10 per cent. benzene; these values are given in

Tables II. to IV. The partial vapour pressures (p) of the components of

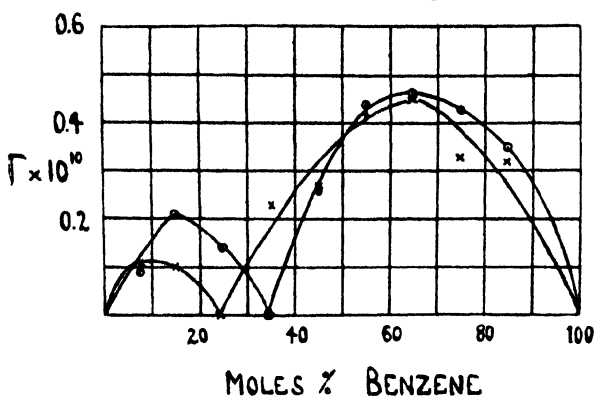


FIG. 1.—Benzene—acetic acid. Benzene adsorbed—acetic acid adsorbed. \times 20° \odot 35°.

mixtures corresponding to these values of surface tension were obtained from data given in the International Critical Tables. These were plotted against moles per cent. of benzene and the required values—given in Tables II. to IV.—read off.

The surface concentration of the component which is positively adsorbed

is given by the Gibbs equation, which may be written in the form,

$$\Gamma = - \frac{1}{RT} \frac{d\gamma}{d \log p}$$

The values calculated in this way are given in Tables II. to IV. in moles per sq. cm. As the values of $\Delta\gamma$ and of $\Delta \log p$ are small, the possible error in Γ will be fairly large, but the accuracy is sufficient to show definitely the form of the adsorption-composition curve. These curves are reproduced in Figs. 1, 2, and 3.

Discussion of Results.

(a) If it is assumed that the adsorbed layer is unimolecular, then the area occupied per molecule in it may be calculated

$$(A = 1/\Gamma N).$$

Table V. gives this area in \AA^2 corresponding to the maxima on the adsorption curves.

These areas are very much greater than those of the adsorbed molecules, and it must be concluded that the surface layer is far from saturation.

(b) The adsorption curve for each of these mixtures is very different. For benzene-acetic acid mixtures the adsorption increases with increasing benzene content, reaches a maximum, and then falls to zero, after which acetic acid is adsorbed, the amount of which also passes through a maximum. In the case of benzene-carbon disulphide, benzene is adsorbed throughout, a maximum being rapidly attained, after which

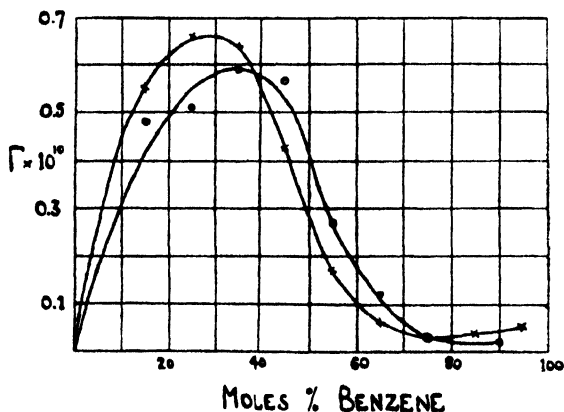


FIG. 2.—Benzene—carbon disulphide. Benzene adsorbed. \times 20° \odot 30°.

the adsorption falls to a very low value. For benzene-carbon tetrachloride the latter component is adsorbed, at first in increasing amount with increasing tetrachloride content; no maximum is, however, observed, but the adsorption tends to a steady value. In view of the large area occupied per molecule, it is improbable that these changes are to be ascribed to changes in the orientation of molecules in the surface layer. The descending portions of the curves may be explained by the formation below the surface layer of a layer relatively rich in the component not adsorbed.

(c) As the adsorbed molecules in the surface film are widely separated, the Traube-Langmuir modification of the gas laws should apply to those mixtures for which the surface

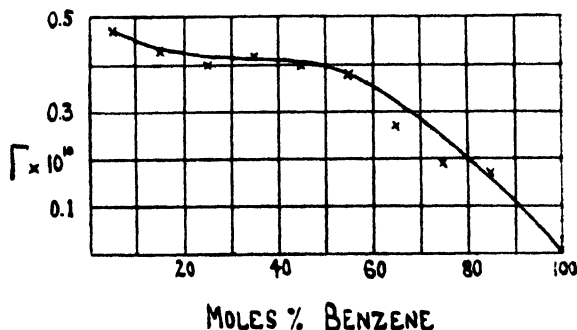


FIG. 3.—Benzene—carbon tetrachloride. 50°. Carbon tetrachloride adsorbed.

tension lowering is proportional to the bulk concentration. The values of FA/RT , where F is the surface tension lowering, $\gamma_0 - \gamma_1$, and A is the area occupied per mole, are given in Table VI. The deviations from unity are considerable. Strictly, F is the difference in the surface tension of the liquid with and without the surface film and this may not be equal to $\gamma_0 - \gamma$; this may give rise to the discrepancy. The lowerings are too small to apply the analogue of Amagat's equation proposed by Schofield and Rideal.²

TABLE V.

Mixture.	Temp.	Substance Adsorbed.	$\Gamma_{\text{MAX}} \times 10^{10}$.	A.
Benzene and (a) Acetic acid.	20°	Benzene.	0.09	1840
		Acetic acid.	0.43	390
	35°	Benzene.	0.22	760
		Acetic acid.	0.43	390
(b) Carbon disulphide.	20°	Benzene.	0.05	250
	30°	Benzene.	0.61	280
(c) Carbon tetrachloride.	50°	Benzene.	0.43	390
		Carbon tetrachloride.		

(d) The influence of temperature is of interest. The minimum in the surface tension-composition curve for benzene-acetic acid corresponds to a higher benzene content at 35° than at 20°. The mixture for which neither component is adsorbed is thus richer in benzene as the temperature increases. The surface tension-composition curves for benzene-carbon disulphide are very similar at 20° and 30°; the maximum adsorption is greater at the lower temperature and corresponds to a mixture of lower benzene content.

² Schofield and Rideal, *Proc. Roy. Soc.* 1925, 109A, 57.

TABLE VI.

Mixture.	Temp.	Substance Adsorbed.	Moles. Per Cent. Benzene.	F.	FA/RT.
(a) Benzene and Acetic acid.	35°	Acetic acid.	85	0.56	0.63
			75	0.89	0.81
			65	1.21	1.06
(b) Carbon disulphide.	20°	Benzene.	15	2.04	1.52
			25	2.67	1.67
	30°	Benzene.	15	1.91	1.58
			25	2.47	1.93
(c) Carbon tetrachloride.	50°	Carbon tetrachloride.	85	0.49	1.07
			75	0.73	1.43
			65	0.95	1.31
			55	1.16	1.13
			45	1.34	1.25
			35	1.52	1.35
			25	1.66	1.54

Summary.

The surface tensions of mixtures of benzene and (a) acetic acid, (b) carbon disulphide, (c) carbon tetrachloride, have been measured and the surface adsorptions calculated from the Gibbs equation. In (a) and (b) the measurements have been made at two temperatures. The form of the adsorption-composition curve and the application of the gas laws to the surface film is discussed.

THE SURFACE TENSIONS OF TERNARY SOLUTIONS. PART III.

BY J. W. BELTON.

Received 1st October, 1935.

In Parts I. and II.¹ the writer has investigated the adsorption of water at the surface of solutions containing two electrolytes and of solutions containing an electrolyte and a non-electrolyte which lowered the surface tension of water. Measurements have now been made on solutions containing an electrolyte and a non-electrolyte which increases the surface tension of water, and on solutions of sodium chloride and dilute hydrochloric acid. Both these systems show features not apparent in those previously studied.

The surface tensions were measured by the bubble pressure method previously described, and were calculated from the relation

$$\gamma = \frac{rg}{2}(h\rho - \frac{2}{3}r\rho_1),$$

where r is the radius of the jet (0.0102 cm.), g is 981.2 cm./sec.², h is the maximum bubble pressure in centimetres of butyl phthalate, ρ is the

¹ Belton, *Trans. Faraday Soc.*, this vol., 1413, 1420.

density of butyl phthalate and ρ_1 the density of the liquid under examination. The solutions were made up by weight from pure chemicals and water of surface tension 72.01 dyne/cm. In the case of the acid-salt mixtures the acid concentration was verified by standardisation. All the measurements were carried out at 25° C.

(a) Sodium Chloride-Sucrose Solutions.

The concentrations of the components were varied so that the mole ratio of sucrose to salt was constant for a single series, this ratio being widely varied for different series. The surface tensions are given in Table I., in which m_1 and m_2 are respectively the number of moles of sucrose and salt per 1000 gms. of water, N_1/N_2 the mole ratio of sucrose to salt and p_{H_2O} the partial vapour pressure of water obtained from the data of Schoorl.¹

The surface concentrations were calculated from the Gibbs equation. Both solutes increase the surface tension of water and consequently only water is positively adsorbed at the surface. It is assumed below that the Gibbs surface may be drawn through this adsorbed layer so that the concentrations of the other components are zero. According to the Gibbs equation

$$\begin{aligned} d\gamma &= -\Gamma_1 d\mu_1 - \Gamma_2 d\mu_2 - \Gamma_3 d\mu_3 \\ &= -\Gamma_1 RT d \log a_1 - \Gamma_2 RT d \log a_2 - \Gamma_3 RT d \log a_3 \end{aligned} \quad (1)$$

where γ is the surface tension Γ_1 , Γ_2 , Γ_3 the surface concentrations, μ_1 , μ_2 , μ_3 the chemical potentials, and a_1 , a_2 , a_3 the activities of the components. If $\Gamma_1 = 0$ and $\Gamma_2 = 0$, then

$$d\gamma = -\Gamma_3 RT d \log a_3 \quad (2)$$

If N_1 , N_2 and N_3 are respectively the mole fractions of sucrose, salt and water, then

$$\left(\frac{\partial \gamma}{\partial N_3} \right)_{N_1/N_2} = -\Gamma_3 RT \left(\frac{\partial \log a_3}{\partial N_3} \right)_{N_1/N_2} = -\Gamma_3 RT \left(\frac{\partial \log p}{\partial N_3} \right)_{N_1/N_2} \quad (3)$$

The values of Γ_3 given in Table I. in moles/cm.² were calculated from

$$\Gamma_3 = -(\Delta\gamma/RT \Delta \log p_{H_2O})_{N_1/N_2} \quad (4)$$

Discussion of Results.

It is not possible from the data in Table I. to discover a relation between the surface adsorption and the composition of the solution. It is of interest, however, to compare the surface tensions and adsorptions with those for solutions containing only sodium chloride or sucrose. It has been found,¹ for solutions containing sodium and potassium chlorides, both of which raise the surface tension of water, that the surface tensions and adsorptions in the mixed solution were approximately the sum of those in separate solutions. For the present system no such additive relation holds. Table II. gives the adsorption for solutions containing only sucrose (Γ_s) and only sodium chloride (Γ_{NaCl}). The sum of these is in all cases considerably greater than the experimental value (Γ_g).

The reason for this reduction in surface adsorption may be the formation of a sucrose-sodium chloride compound in the solution—the existence of the compound $C_{12}H_{22}O_{11}$, $NaCl$, $2H_2O$ has been deduced

¹ Schoorl, *Rec. Trav. Pays.-Bas*, 1923, **42**, 790.

TABLE I.

	N_1/N_2	m_1	m_2	k	γ	P_{H_2O}	$\Gamma \times 10^3$
Series 1	0.063	0.131	2.00	14.48	75.59	22.3	1.2
		0.167	2.63	14.67	76.59	21.6	1.4
		0.292	4.60	15.305	79.91	19.7	
Series 2	0.187	0.837	4.49	15.30	78.30	19.9	2.2
		1.11	5.94	15.67	81.78	18.7	
Series 3	0.487	1.74	3.59	15.15	79.08	20.6	1.0
		2.09	4.28	15.335	80.04	19.9	1.3
		2.64	5.42	15.74	82.16	18.7	
Series 4	0.589	1.18	2.00	14.855	77.57	22.2	1.3
		1.64	2.86	15.18	79.25	21.1	1.8
		2.31	3.93	15.455	80.67	20.4	
Series 5	0.918	1.30	1.40	14.705	76.77	22.4	2.3
		1.92	2.08	15.02	78.41	21.8	0.7
		3.78	4.11	15.41	80.43	19.4	
Series 6	1.748	1.88	1.06	14.62	76.33	22.6	0.9
		2.74	1.56	14.845	77.52	21.4	1.2
		4.21	2.41	15.14	79.02	20.4	
Series 7	3.40	2.05	0.61	14.545	75.94	22.3	2.2
		2.96	0.87	14.705	76.77	21.9	0.8
		4.16	1.22	14.96	78.10	20.6	0.7
		5.25	1.54	15.12	78.93	19.7	

from vapour pressure measurements. The water layer on the surface of a salt solution may be due to the presence of hydrated ions near the surface and that on a sucrose solution to hydrated sucrose molecules. In the mixed solution the surface layer would be due to the hydrated complex. This would explain why the adsorption is of the order of that on the sodium chloride solution rather than the sum of the two separate solutions. In the case of sodium chloride-potassium chloride solutions no such complex is formed and each sol-

TABLE II.

Series.	Γ_S	Γ_{NaCl}	$\Gamma_S + \Gamma_{NaCl}$	Γ_3
1	3.8	1.6	5.4	1.2
	3.1	1.4	4.5	1.4
2	1.9	1.3	3.2	2.2
3	1.6	1.4	3.0	1.0
	1.6	1.4	3.0	1.3
4	1.8	1.5	3.3	1.3
	1.6	1.4	3.0	1.8
5	1.7	1.6	3.3	2.3
	1.5	1.4	2.9	0.7
6	1.6	1.5	3.1	0.9
	1.4	1.6	3.0	1.2
7	1.5	1.9	3.4	2.2
	1.4	1.8	3.2	0.8
	1.3	1.7	3.0	0.7

ute contributes its quota to the surface layer.

(b) The Influence of Dilute Hydrochloric Acid on the Surface Tensions of Sodium Chloride and Potassium Chloride Solutions.

The surface tension of 0.1M hydrochloric acid is only 0.02 dyne/cm. less than that of pure water, and it might be expected that its presence

in strong solutions of salts could therefore be neglected. This would be so if the surface tension change for the mixture were the sum of the changes each solute would produce if present separately. This simple additive relation does not apply to mixtures of sodium chloride and hydrochloric acid of strength 1.5*M*, nor does it apply the solutions described below.

The surface tensions of solutions containing sodium chloride and 0.1*M* acid and potassium chloride and 0.1*M* acid are given in Table III., in which m_1 and m_2 are the number of moles of salt and of acid per 1000 gms. of water, h is the maximum bubble pressure in centimetres of butyl phthalate, and $\Delta\gamma_{12}$ is the surface tension increment. The sixth column gives this increment calculated from the relation

$$\Delta\gamma_{12} = k_1 m_1 + k_2 m_2 \quad (5)$$

where k_1 and k_2 are the increments for unit concentration change for acid and salt respectively. The values of $\Delta\gamma_{12}$ in the final column were calculated from

$$\Delta\gamma_{12} = k_1 m_1 + k_2 m_2 + k_3 m_1 m_2^{\frac{1}{2}} \quad (6)$$

where k_3 is a constant equal to -0.5 for sodium chloride (*cf.* Pt. I.) and -0.28 for potassium chloride. This relation gives good agreement with the observed values, as it was found to do for the stronger acid-salt solutions.

It was shown in the previous paper that the ratio of the adsorption in the mixed solution (Γ_1) to that in a solution containing only salt (${}_0\Gamma_1$) is given by

$$\frac{\Gamma_1}{{}_0\Gamma_1} = 1 + \frac{k_3 m_2^{\frac{1}{2}}}{k_1} + \Gamma_2 \frac{2RT}{k_1} \frac{\partial \log f_2}{\partial m_1} \quad (7)$$

The activity coefficients of hydrochloric acid (f_2) in acid-salt mixtures have been found by Harned,³ who gives

$$\log f = \alpha m_1 - \beta(m_1 + m_2)^{\alpha'} + \alpha'' m_2 \quad (8)$$

where α , β , α' , and α'' are empirical constants. Calculation shows that $\partial \log f_2 / \partial m_1$ is small and that the third term in (7) may be neglected. Table IV. gives the ratio $\Gamma_1 / {}_0\Gamma_1$ calculated in this way, the thickness of the aqueous layer on the corresponding pure salt solution (${}_0\delta$) and that on the mixed solution (δ_{12}). It will be observed that the addition of a

TABLE III.

m_1	m_2	h	γ_{12}	$\Delta\gamma_{12}$ obs.	$\Delta\gamma_{12}$	$\Delta\gamma_{12}$
(a) Sodium Chloride and Hydrochloric Acid.						
1.005	0.1	14.12	73.69	1.68	1.79	1.57
2.014	0.1	14.405	75.18	3.17	3.45	3.13
3.025	0.1	14.705	76.74	4.73	5.12	4.72
4.031	0.1	15.01	78.34	6.33	6.85	6.23
5.035	0.1	15.315	79.94	7.93	8.54	7.74
(b) Potassium Chloride and Hydrochloric Acid.						
1.015	0.1	14.10	73.60	1.59	1.68	1.61
2.018	0.1	14.365	74.98	2.79	3.33	3.15
3.032	0.1	14.665	76.52	4.51	4.60	4.33
4.033	0.1	14.88	77.69	5.68	6.14	5.78

³ Harned, *J. Amer. Chem. Soc.*, 1922, 44, 2729.

relatively small amount of acid, which alone has an effect on the surface tension of water of the order of the experimental error, produces a marked change in the amount of water adsorbed at the surface of a salt solution.

TABLE IV.

m_1	m_2	h_1	Γ_1/Γ_1^0	θ	δ_{1s}
(a) Sodium Chloride and Hydrochloric Acid.					
1	0.1	1.7	0.91	4.06	3.69
2	0.1	1.7	0.91	3.15	2.86
3	0.1	1.7	0.91	2.70	2.46
4	0.1	1.7	0.91	2.39	2.18
5	0.1	1.7	0.91	2.11	1.92
(b) Potassium Chloride and Hydrochloric Acid.					
1	0.1	1.67	0.95	3.78	3.59
2	0.1	1.65	0.95	3.44	3.27
3	0.1	1.55	0.95	2.94	2.76
4	0.1	1.53	0.95	2.62	2.46

Summary.

The surface tensions of solutions containing (a) sucrose and sodium chloride and (b) dilute hydrochloric acid and sodium chloride and dilute hydrochloric acid and potassium chloride have been measured and the surface adsorptions of water calculated. In the former the adsorptions are much less than the sum of the adsorptions each solute would produce separately. In the latter an amount of acid which has hardly any effect on the surface tension of water produces a marked effect on the adsorption of water on a salt solution.

THEORY OF ADSORPTION.

BY H. BRADLEY.

Received 1st October, 1935.

In a recent paper¹ S. Miyamoto proposes an adsorption theory in which he assumes that of the molecules in the gas phase only those can be adsorbed which strike the surface of the adsorbent with velocities whose components perpendicular to the surface are greater than a limiting value u_0 ; and only those molecules can escape from the adsorbed layer whose energies (of vibration perpendicular to the surface or translatory motion upon it) are greater than a limiting value ϵ_0 . The formula derived for the amount of adsorbed material is:

$$a = \frac{N_0}{N} \cdot \frac{Kp^{1/n}}{1 + Kp^{1/n}} \text{ mol./sq. cm.}$$

in which a and p have their usual significance. N_0 is the number of adsorbing points per unit surface, N is Avogadro's number, K is a coefficient varying with temperature and n is an exponent also varying with temperature.

It is of importance to note that the exponent n is introduced by another essential assumption. Let it be that at any instant a number x of the

¹ S. Miyamoto, *Kolloid Z.*, 1935, 70.

total N_0 adsorbing points are satisfied. The number of adsorbed molecules which approach a unit area of the surface and which fulfil the required energy condition Miyamoto finds to be :

$$R_0 = \frac{Np}{\sqrt{2\pi MRT}} e^{-\frac{Mu_0^2}{2RT}} \text{ mol./sq. cm./sec.}$$

The amount adsorbed is

$$R = f_1 R_0 \text{ mol./sq. cm./sec.}$$

The important assumption is that

$$f_1 = \left(1 - \frac{x}{N_0}\right)^n.$$

Similarly for the molecules escaping from the adsorbed layer

$$E = f_2 E_0$$

where it is assumed that

$$f_2 = \left(\frac{x}{N_0}\right)^n.$$

Still more recently R. H. Fowler,² by the application of Fermi-Dirac statistical methods, has derived Langmuir's adsorption isotherm; and for the case where each adsorbed molecule requires two points of attachment he obtains the expression

$$\theta = \frac{(Ap)^{\frac{1}{2}}}{1 + (Ap)^{\frac{1}{2}}},$$

where θ = fraction of surface of solid covered by adsorbed molecules. The analysis involves the assumption that the fields holding the adsorbed molecules are independent of temperature.

These two instances prompt the author to draw attention once again to the formula which he put forward more than eight years ago.³

$$a = \frac{\alpha p^{T/273x}}{1 + \beta p^{T/273x}},$$

T is, as usual, the absolute temperature; x is an integer, frequently unity, though sometimes 2, or 3 as the examples given below illustrate.

This formula is, of course, identical with Miyamoto's with the additional advantage that the value of the exponent n is given. Miyamoto does not give in his paper any examples of the application of the formula to experimental results and, in fact, if the three quantities N/N_0 , K and n are all unknown constants, it is not a very simple matter to find their best values for a given set of experimental data. When $n = T/273x$ the formula becomes one with only two unknown constants and the application to experimental results simply involves the plotting of $1/a$ against $1/p^{T/273x}$ and testing for rectilinearity. A few trials with x successively equal to 1, 2, 3, etc., quickly lead to a conclusion.

The formula has been applied with a high degree of success to a wide variety of published experimental results. The exigencies of space would not allow the inclusion in this paper of all the applications that have been made; but perhaps a few examples may be permitted to illustrate how satisfactorily the formula can represent experimental observations.

² R. H. Fowler, *Proc. Cambridge Phil. Soc.*, 1935, 31.

³ H. Bradley, *Nature*, 1927, 120, 82.

In the following tables p (pressure) is given in centimetres of mercury. The amount adsorbed, a , is the gas volume expressed in cubic centimetres and reduced to 0°C . 760 mm. adsorbed by 1 gram of adsorbent.

ADSORPTION OF CARBON MONOXIDE ON COCONUT CHARCOAL.⁴

1. At -78.5°C . $\alpha = 9.901$;
 $\beta = 0.1376$; $x = 1$; $T/273x = 0.712$.

p .	a (obs.).	a (calc.).
4.0	19.4	19.40
7.2	25.7	25.86
11.7	31.7	31.82
14.8	34.7	34.80
18.7	37.6	37.70
28.8	43.4	43.24
44.2	49.3	48.30

2. At -33.6°C . $\alpha = 1.353$;
 $\beta = 0.0267$; $x = 1$; $T/273x = 0.8768$.

p .	a (obs.).	a (calc.).
10.1	8.54	8.54
18.8	13.10	13.13
32.0	18.20	18.12
43.0	21.00	21.13
54.0	23.80	23.75
67.0	26.30	26.14

3. At 0°C . $\alpha = 0.3448$; $\beta = 0.01063$;
 $x = 1$; $T/273x = 1$.

p .	a (obs.).	a (calc.).
7.3	2.34	2.34
18.0	5.17	5.25
30.4	7.84	7.91
54.0	11.90	11.82
88.2	16.50	15.66

4. At 20°C . $\alpha = 0.1626$;
 $\beta = 0.00698$; $x = 1$; $T/273x = 1.074$.

p .	a (obs.).	a (calc.).
12.3	2.19	2.18
30.0	4.80	4.93
49.5	7.27	7.34
85.6	11.00	10.56

5. At 46.2°C . $\alpha = 0.0625$;
 $\beta = 0.000443$; $x = 1$; $T/273x = 1.169$.

p .	a (obs.).	a (calc.).
21.4	1.94	1.94
50.9	4.22	4.30
83.5	6.34	6.26

ADSORPTION OF ARGON BY COCONUT CHARCOAL.⁵

1. At -78.3°C . $\alpha = 3.256$;
 $\beta = 0.0224$; $x = 1$; $T/273x = 0.713$.

p .	a (obs.).	a (calc.).
5.42	9.9	10.11
9.84	15.4	14.92
12.90	18.6	17.72
21.80	24.0	24.41
29.50	28.8	29.08
56.40	39.4	41.33
75.80	46.9	47.5

2. At -37°C . $\alpha = 0.7696$;
 $\beta = 0.01386$; $x = 1$; $T/273x = 0.8644$.

p .	a (obs.).	a (calc.).
30.96	11.84	11.78
41.70	14.23	14.35
56.84	17.02	17.38
81.50	21.88	21.30

3. At 0°C . $\alpha = 0.1713$;
 $\beta = 0.004111$; $x = 1$; $T/273x = 1$.

p .	a (obs.).	a (calc.).
8.16	1.350	1.35
19.70	3.157	3.12
26.60	4.257	4.11
58.00	7.980	8.01
79.70	10.370	10.28

ADSORPTION OF NITROGEN ON CHARCOAL.⁶

At 0°C . $\alpha = 0.2564$; $\beta = 0.006744$; $x = 1$;
 $T/273x = 1$.

p .	a (obs.).	a (calc.).
0.43	0.111	0.110
1.21	0.298	0.308
3.93	0.987	0.982
12.98	3.040	3.059
22.94	5.080	5.094
34.01	7.050	7.092
56.23	10.310	10.460
77.46	13.050	13.040

⁴ Freundlich, *Colloid and Capillary Chemistry*, translated Hatfield, London, 1926, pp. 116.

⁵ Miss I. F. Homfay, *Z. physik. Chem.*, 1910, 74, 129.

⁶ Titoff, *Z. physik. Chem.*, 1910, 74, 641.

ADSORPTION OF WATER VAPOUR BY COTTON.⁷

In this case it is found necessary to put $x = 2$ for the first half of the adsorption isotherm and $x = 4$ for the second half. Also β has a negative value, as is to be expected.

In the following table pressures are given as fractions of saturation pressure and the amounts adsorbed are per unit weight of the cotton.

At 20° C. $\alpha = 0.05883$; $\beta = -0.4465$; $x = 2$; $T/273x = 0.5365$.			$\alpha = 0.01389$; $\beta = -0.9208$; $x = 4$; $T/273x = 0.2683$.		
p .	a (obs.).	a (calc.).	p .	a (obs.).	a (calc.).
0.050	0.0139	0.0130	0.710	0.0821	0.0798
0.100	0.0196	0.0197	0.794	0.0982	0.0984
0.198	0.0304	0.0304	0.844	0.1106	0.1128
0.294	0.0402	0.0398	0.874	0.1210	0.1210
0.408	0.0495	0.0503	0.894	0.1274	0.1285
0.500	0.0581	0.0588	0.952	0.1574	0.1530
0.556	0.0624	0.0640	0.972	0.1770	0.1625
0.598	0.0679	0.0676			

It is noteworthy that in all cases of the adsorption of water vapour it has been found necessary to make $x = 2$ or a multiple of 2. This also applies to cases of adsorption of a solute from aqueous solution, as the following examples show. In the case of adsorption from solution in benzene $x = 3$.

In the tables which follow the concentration C is in mol. per litre, the amount adsorbed is in millimol per gram of carbon.

ADSORPTION OF ACETONE IN WATER ON BLOOD CHARCOAL AT 18° C.⁸

$$\alpha = 6.024; \beta = -0.245; x = 2; T/273x = 0.533.$$

C .	a (obs.).	a (calc.).
0.00234	0.208	0.237
0.01465	0.618	0.619
0.04103	1.075	1.053
0.08862	1.500	1.554
0.17759	2.080	2.190
0.26897	2.880	2.667

ADSORPTION OF BROMINE IN WATER ON BLOOD CHARCOAL AT 0° C.¹⁰

$$\alpha = 82.64; \beta = 7.02; x = 2; T/273x = 0.5.$$

C .	a (obs.).	a (calc.).
0.00092	2.07	2.07
0.00259	3.10	3.10
0.00669	4.27	4.29
0.01708	5.44	5.64
0.02975	6.80	6.45

ADSORPTION OF ISOAMYL ALCOHOL IN WATER ON BLOOD CHARCOAL AT 15° C.⁸

$$\alpha = 8.130; \beta = 0.04065; x = 4; T/273x = 0.264.$$

C .	a (obs.).	a (calc.).
0.0125	2.52	2.529
0.0225	2.95	2.945
0.1100	4.45	4.444

ADSORPTION OF BENZOIC ACID IN BENZENE ON BLOOD CHARCOAL AT 25° C.¹¹

$$\alpha = 2.809; \beta = 0.216; x = 3; T/273x = 0.364.$$

C .	a (obs.).	a (calc.).
0.00618	0.437	0.447
0.02500	0.780	0.778
0.05313	1.040	1.044
0.11770	1.440	1.433

The value which has to be assigned to x may turn out to be of important significance, and it is a point especially worth attention in view of the work of Fowler referred to at the outset of this paper wherein $\frac{1}{2}$ is derived as the index of pressure under certain conditions.

⁷ Orme Masson and E. S. Richards, *Proc. Roy. Soc.*, 1907, 78A, 412.

⁸ Freundlich, *loc. cit.*,⁴ p. 173 from expt. by Michaelis and Rowe.

⁹ *Ibid.* from expts. by van Duin.

¹⁰ *Ibid.*, p. 174.

¹¹ *Ibid.*

THE HYDROGEN PEROXIDE THEORY OF ELECTROLYTIC OXIDATION AND THE INFLUENCE OF THE ELECTRODE SURFACE ON ANODIC PROCESSES.

BY S. GLASSTONE AND A. HICKLING.

Received 27th August, 1935.

In order to account for the anodic phenomena observed in the electrolytic oxidation of thiosulphate, sulphite and acetate ions, and in the electrolysis of halide solutions, the present authors put forward the suggestion that hydrogen peroxide is primarily formed at an anode by the union of discharged hydroxyl radicals.¹ In a recent paper O. J. Walker and Weiss² have adversely criticised this view and, after giving reasons for believing that hydrogen peroxide cannot be formed at an anode under the conditions of the electrolytic experiments, have proposed an alternative theory, with particular reference to the formation of ethane (Kolbe reaction) and of methyl alcohol (Hofer-Moest reaction) by the oxidation of acetate; the theory is considered to apply equally to the oxidation of thiosulphate and sulphite ions. It is suggested that at an electrode of low overvoltage hydroxyl-ion discharge is the first process to occur, the radicals reacting with acetate ions to yield methyl alcohol; at high overvoltage anodes acetate ions are supposed to be preferentially discharged and the radicals are then said to react to give ethane and carbon dioxide. Quite apart from the fact that the arguments against the possibility of the formation of hydrogen peroxide are by no means conclusive, and that the alternative theory encounters many difficulties, to be considered later, an examination of some of the data in the literature³ indicated that the relationship between the efficiency in the reactions under consideration and the oxygen overvoltage at various anodes was by no means as exact as Walker and Weiss implied. It appeared desirable, therefore, to measure overvoltages at a number of anodes under such conditions that the results might be comparable with one another and with the known oxidation efficiencies⁴ at those electrodes.

Experimental.

The minimum overvoltages, at which oxygen evolution commences, were difficult to measure, and so observations were made at a series of increasing *C.D.*'s; as a general rule the anode was polarised at the *C.D.* quoted for one to two minutes before the potential was measured. For the lower *C.D.*'s the direct method was used, but for the highest current the commutator-extrapolation principle was employed.⁴ The anodes, each of 2 sq. cm. apparent area, were as follows: (A) smooth platinum; (B) platinised platinum; (C) platinised platinum polarised for 30 minutes

¹ *J. Chem. Soc.*, 1932, 2345, 2800; 1933, 829; 1934, 10, 1772, 1878.

² *Trans. Faraday Soc.*, 1935, 31, 1011.

³ Coehn and Osaka, *Z. anorg. Chem.*, 1903, 34, 86; Foerster and Piguet, *Z. Elektrochem.*, 1904, 10, 74; Newbery, *J. Chem. Soc.*, 1916, 109, 1066; Knobel, Caplan and Eiseman, *Trans. Amer. Electrochem. Soc.*, 1923, 43, 55.

⁴ *J. Chem. Soc.*, 1924, 125, 250; 1927, 641.

in *N*-sodium hydroxide solution at 0.25 amp./sq. cm.; (D) platinised platinum deposited from a solution containing 0.01 *M*-mercuric chloride; (E) gold; (F) smooth platinum covered with a thin adherent film of lead dioxide by electrolysis of a solution of *N*-potassium acetate, *N*-acetic acid and 0.1 *M*-lead acetate; (G) the same as F, but covered with manganese dioxide by the use of manganous acetate in place of lead acetate; (H) arc gas-carbon, and (I) nickel. The cathode was a platinum wire in each case, enclosed in a filter "candle," so that anode and cathode compartments were separated. In order to avoid possible complications resulting from the presence of other anions the electrolyte used was *N*-sodium hydroxide. The results obtained at room temperature (about 17°) are given in the table below; the efficiencies at the various anodes for the Kolbe reaction, and for the formation of tetrathionate and dithionate in solutions of p_H 7, are also quoted.

TABLE.—OXYGEN OVERVOLTAGES IN *N*-NaOH AT 17°.

C.D. Amp./Sq. Cm. $\times 10^4$.	A.	B.	C.	D.	E.	F.	G.	H.	I.
5	0.45	0.30	0.44	0.31	0.86	0.46	0.70	—	0.19
10	0.50	0.32	0.47	0.34	0.92	0.48	0.73	—	0.22
20	0.57	0.34	0.50	0.37	0.95	0.51	0.76	—	0.24
40	0.65	0.36	0.52	0.40	0.97	0.54	0.78	0.35	0.26
750	0.85	0.46	0.67	0.51	1.00	0.73	0.88	0.58	0.40
Efficiency.	A.	B.	C.	D.	E.	F.	G.	H.	I.
Kolbe reaction	89	3	(36)	42	0	0	0	21	0°/0
S ₂ O ₆ '' formation	76	91	—	—	65	—	0	51	60
S ₂ O ₆ '' formation	28	7	—	—	28	—	2	3	32

Discussion.

An examination of the efficiencies for the three oxidation processes and the overvoltages of the various anodes fails to reveal any parallelism between the two properties. It is true that as a result of prolonged oxygen evolution at relatively high *C.D.*'s the overvoltage of a smooth anode rises, but it is improbable that a similar change occurs, at least during the early stages, in any of the electrolyses studied when the oxygen evolution is quite negligible. From these results it appears very improbable that oxidation efficiencies for the Kolbe reaction and for the formation of tetrathionate and dithionate can be correlated in a simple manner with the overvoltage properties of the electrode surface.

One of the fundamental bases of the theory of Walker and Weiss is that "in general, conditions will be more favourable to the discharge of any anion present than for the OH' ion, as the electron affinity of the latter exceeds the electron affinities of other anions." The last part of this statement is open to question, but in any case this view implies that in the electrolysis of acid solutions, for example, the anions are discharged at a platinum anode in preference to hydroxyl ions; it is well known, however, that oxygen evolution commences at the same potential in *N*-solutions of various acids, and that the overvoltage is the same as in a solution of sodium, or other alkali hydroxide,⁵ wherein

⁵ This can be deduced from the results of Le Blanc, *Z. physikal. Chem.*, 1891, 8, 299; 1893, 12, 333.

hydroxyl-ion discharge is the *sole* anodic process. These facts imply, even if anions are primarily discharged, which is doubtful, that in every case the *rate determining reaction* is the process $\text{OH}' \rightarrow \text{OH} + e$ (electrode). In the electrolysis of acetate solutions oxygen can be obtained with high efficiency at low *C.D.*'s;⁶ the potentials are then clearly sufficient for hydroxyl-ion discharge to occur, yet when the *C.D.* is increased the potential rises and the Kolbe reaction takes place, it must be postulated, according to Walker and Weiss, that hydroxyl ions are no longer discharged! A similar difficulty arises when comparing the anode potentials of platinum during the Kolbe reaction with the (lower) values when oxygen is being evolved at the same electrode in solutions of the same p_{H} not containing acetate.⁷ The potentials in the former case are evidently sufficient for the oxygen overvoltage at smooth platinum to be markedly exceeded, but the amount of oxygen evolved is almost negligible.

Further, if, owing to the high overvoltage at platinum, acetate-ion discharge occurs in preference to hydroxyl-ion discharge, how is it that the Hofer-Moest reaction, which is supposed to involve the latter process, replaces the Kolbe reaction when neutral salts are added to acetic acid solutions? In view of the arguments just presented it can hardly be said that the anions of the neutral salts are preferentially discharged, but even so, it is unlikely that the ferricyanide ion would be discharged more readily than the chlorine ion, as the experimental results would imply.⁷ It may also be noted that the efficiency for the Kolbe reaction in a 2*N*-acetic acid solution, p_{H} about 3, is 71 per cent., whereas in 2*N*-potassium acetate and 0.1*N*-ammonium hydroxide, p_{H} about 11, it is still at least 50 per cent., in spite of the hydroxyl-ion discharge potential being theoretically 0.46 volt lower in the latter case.

Similar difficulties with regard to the anode potentials arise in connection with the oxidation of thiosulphate and of sulphite ions, and in the electrolysis of halide solutions, if it is supposed that the formation of tetrathionate, dithionate or halogen respectively, is due only to the direct discharge of the appropriate ions. In every case the addition of manganous sulphate to the electrolyte, which probably results in the incipient deposition of manganese dioxide on the anode, brings about a marked *increase* of potential, but the essential oxidation process is always entirely inhibited or considerably diminished in extent. In thiosulphate solutions, for example, the potentials at platinised platinum and nickel anodes, which have the lowest overvoltages (p. 1657), are low but the oxidation efficiencies are high; in the presence of manganese ions, however, giving possibly a manganese dioxide anode, the potentials are very high but the whole of the current is devoted to oxygen evolution. If the $\text{S}_2\text{O}_3''$ ion can be discharged at the low potentials, then why not at the higher? Similar phenomena have been observed in sulphite and halide solutions, and are equally difficult to account for on the basis of the direct discharge of ions, without the erection of various subsidiary hypotheses of a speculative nature.

In addition to the anode potential observations there are many other facts which are by no means easy to explain. The deposition of oxides on anodes, noted by Walker and Weiss, has frequently been observed by the present authors, during the electrolysis of solutions

⁶ See, for example, Shukla and O. J. Walker, *Trans. Faraday Soc.*, 1931, **27**, 722.

⁷ Glasstone and Hickling, *J. Chem. Soc.*, 1934, 1878.

containing lead, manganese and silver salts;⁸ but with iron and copper salts, in neutral and acid solutions, it is doubtful whether such oxides are formed, yet the efficiencies of oxidation processes are definitely decreased by these substances. It may perhaps be emphasised that the theory of the primary anodic formation of hydrogen peroxide was originally put forward to account for the fact that such varied substances are arsenious oxide, strychnine and copper sulphate are able to inhibit the anodic oxidation of thiosulphate to tetrathionate;⁹ the experiments with other catalysts for hydrogen peroxide decomposition served to confirm the conclusion reached. It is of interest to note, in further support of the theory originally proposed, that the action of hydrogen peroxide is in a large number of cases qualitatively similar to that brought about by electrolytic oxidation.¹⁰

The influence of p_H , especially with a gold anode, of ammonium molybdate on the relative amounts of tetrathionate and sulphate formed, and of *solid* catalysts for hydrogen peroxide decomposition on the efficiency of thiosulphate oxidation, are not easily accounted for on the basis of anodic overvoltages and the supposition that thiosulphate ions are primarily discharged. A careful perusal of the literature shows that in the electrolysis of acetate, thiosulphate, sulphite and halide solutions there are many other phenomena which are equally difficult to explain by the aforementioned theory.

The present authors claim that all the complex phenomena fall readily into line with the view that hydrogen peroxide is primarily formed at an anode: the chief objection of Walker and Weiss to the essential postulate is, however, that "hydrogen peroxide is certainly not formed" under the conditions of the electrolytic experiments.¹¹ The fact that the peroxide *can be detected* under unusual conditions (-40°C.), when hydroxyl-ion discharge is the only reasonable anodic process, surely implies that its formation at an anode under normal conditions is not *impossible*. The work of Rodebush and Wahl¹² and of Oldenberg¹³ appears to prove quite conclusively that hydroxyl radicals do actually combine in the gas phase to yield hydrogen peroxide, and there seems no fundamental reason for objecting to the suggestion that the same process occurs in solution. Solid materials certainly act catalytically in decomposing the peroxide, but it is not improbable that when an alternative process, *e.g.*, oxidation, is possible, some of the peroxide will take part in it. Further, the formation of hydrogen peroxide in solution in amounts corresponding with the requirements of Faraday's laws, by electrolysis with a glow discharge electrode when the anode, *but not the cathode*, is in the gas space,¹⁴ cannot be lightly dismissed. Finally the recent work of Klemenc and Kantor¹⁵ also implies that hydrogen peroxide can be formed in solution by the union of discharged hydroxyl radicals.

Whilst we should welcome an alternative theory which would account for the facts of electrolytic oxidation in a simple manner, we prefer to

⁸ Cf. Glasstone and Hickling, *J. Chem. Soc.*, 1932, 2352.

⁹ *Ibid.*, p. 2351.

¹⁰ See Fichter *et al.*, *Ber.*, 1914, 47, 2006; *Helv. Chim. Acta*, 1918, 1, 297; Glasstone and Hickling, *J. Chem. Soc.*, 1932, 2355.

¹¹ Walker and Weiss, *Trans. Faraday Soc.*, 1935, 31, 1012.

¹² *J. Chem. Physics*, 1933, 1, 696.

¹³ *Ibid.*, 1935, 3, 266.

¹⁴ Glasstone and Hickling, *J. Chem. Soc.*, 1934, 1773.

¹⁵ *Z. physikal. Chem.*, 1934, 27B, 359.

adopt as a working hypothesis one which does harmonise with experimental observations rather than one apparently at some variance with them. It must be clearly understood, however, we do not imply that all anodic oxidations are due to hydrogen peroxide; many processes take place with the highest efficiency at platinised platinum and lead dioxide anodes, whereas others occur with efficiencies corresponding to the overvoltages of the electrode materials.¹⁶ The mechanisms in such cases are undoubtedly different from that operative in the electrolysis of acetate, thiosulphate or sulphite solutions.

Summary.

(1) Anodic overvoltages have been determined at smooth platinum, platinised platinum, untreated and treated in various ways, gold, manganese and lead dioxide, arc gas-carbon and nickel electrodes. The results show that overvoltages cannot be correlated in any simple manner with the efficiencies in the oxidation of acetate, thiosulphate and sulphite ions.

(2) Some difficulties of the discharged-ion theory of anodic processes are pointed out, and it is shown that the formation of hydrogen peroxide in solution by the union of hydroxyl radicals is not improbable.

(3) It is emphasised that no one mechanism is likely to account for all the various types of anodic oxidation reactions.

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¹⁶ See forthcoming book, *Electrolytic Oxidation and Reduction*, by S. Glasstone and A. Hickling, pp. 336-8, 350.

HOMOGENEOUS CATALYSIS: THE DECOMPOSITION OF ACROLEIN CATALYSED BY IODINE.

BY H. W. THOMPSON AND J. J. FREWING.

Received 11th October, 1935.

Examples of homogeneous catalysis in gaseous processes have multiplied in recent years. One class of reaction, the thermal decomposition of aldehydes, ethers, nitrous oxide, and certain other substances, induced by small amounts of iodine vapour, has been much studied.¹ In general the catalysed decompositions occur at much lower temperatures than the uncatalysed ones, and in the presence of iodine the energy of activation is noticeably lower. The catalyst appears to bring about a simplification of the mechanism, for whereas in general the participation of many degrees of freedom has to be invoked to explain the rates of the uncatalysed decompositions, in the presence of iodine two are usually adequate. The relationship between the rate of reaction and the concentration of aldehyde, or ether, etc., and iodine varies in the different examples. The significance of this has been discussed by Bairstow and Hinshelwood.¹ This "order" with respect to iodine, is of some importance, since proportionality between the rate of reaction and the square root of the iodine

¹ See e.g., Bairstow and Hinshelwood, *Proc. Roy. Soc.*, 1933, **142A**, 77; *J.C.S.*, 1933, 1155; Verhoek and Hinshelwood, *Proc. Roy. Soc.*, 1934, **146A**, 334; and Hinshelwood, *Kinetics of Chemical Change*.

concentration might suggest that free atoms rather than molecules are the effective catalysts.

In a previous paper measurements on the kinetics of the thermal decomposition of acrolein vapour were described.² As then suggested, differences found between this case of an unsaturated molecule, containing moreover a system of conjugated double linkages, and the case of saturated aldehydes previously examined, may be attributable to this structural difference. The present paper deals with the same decomposition catalysed by iodine. Although the analysis of the kinetics and molecular statistics of the process is rather complicated by condensations and secondary reactions, several conclusions are already clearly established.

Experimental Procedure.

The apparatus and method were essentially the same as previously described. Iodine was introduced into the reaction vessel as isopropyl iodide which was allowed a few minutes to decompose completely. Propane and propylene formed in the process $2C_3H_7I = C_3H_8 + C_3H_6 + I_2$ were not present in sufficient quantity (max. 5 per cent. of total pressure) to affect either the reaction velocity or the "end-point." In the gas analyses unsaturated hydrocarbons other than ethylene were absorbed by concentrated sulphuric acid, ethylene by concentrated mercuric acetate solution, carbon monoxide by ammoniacal cuprous chloride and the residue dealt with as previously described. Two reaction vessels were used, both of quartz, one cylindrical and of ca. 200 c.cm. capacity, the other a similar vessel packed with quartz tubing. The relative surface-volume ratio of the two vessels was about fivefold.

Products and Course of the Reaction.

Much condensation to a black tarry deposit accompanies the catalysed decomposition of acrolein, which occurs at much lower temperatures than in the absence of catalyst. The increase of pressure using an initial pressure of 40 mm. amounts to ca. 65 per cent. of the original and falls to ca. 45 per cent. with an initial pressure of 500 mm. These figures are lower than the corresponding ones for the uncatalysed decomposition, which agrees with the much greater extent of condensation, especially at the higher pressures. The products of decomposition are the same and in roughly the same proportions as in the uncatalysed decomposition except that more ethylene appears to be formed at the expense of butylene.

The products would be in accordance with the superposition of two concurrent processes,



and

but as in the uncatalysed reaction there must be additional processes of secondary importance.

As the initial pressure is decreased, the proportion of ethylene among the products increases slightly, which agrees with the bigger "end-point."

TABLE I.

p_0 mm.	"Butylene"	Ethylene.	CO.	"Residue."
103	11.0	19.4	55.6	14.0
203	10.2	16.2	60.4	13.2
297	10.3	15.9	60.8	13.0
402	10.5	15.7	62.1	11.7

² *J.C.S.* (1935), 1443.

Table I. shows analyses of the final products for different initial pressures at 388° C., 4 mm. catalyst were used in each case. During the course of an individual run the proportions of the products remain approximately constant, which implies that secondary processes are at any rate not extensive. In the experiments of Table II. the initial pressure of catalyst was in each case 4 mm., and the temperature 388° C.

TABLE II.

Initial Pressure Acrolein, mm.	Per Cent. Change.	" Butylene."	Ethylene.	CO.	" Residue."
200	20	9.7	17.8	58.5	14.0
	40	10.3	15.5	60.4	13.8
	100	10.0	16.6	60.0	13.4
400	20	10.8	13.1	62.8	13.3
	90	10.5	15.7	62.1	11.7

Curves showing the course of typical runs at 390° C. are shown in Fig. 1.

As in the uncatalysed decomposition it was desirable to determine by chemical analysis how far the rate of pressure change could be regarded as a measure of the rate of disappearance of the acrolein. The method of

TABLE III.

Initial Pressure Acrolein, mm.	Pressure Increase for Half-change in Titre ($\Delta p_{\frac{1}{2}}$).	$\Delta p_{\frac{1}{2}}$ as Percentage of Initial Pressure	$\Delta p_{\frac{1}{2}}$ as Percentage of Total Pressure Increase.
100	28.5	28.5	49
200	43.0	21.5	42
300	55.5	18.5	38
400	62.0	15.5	35

titration using iodine and sodium bisulphite was as previously described (*loc. cit.*), a small allowance being made here for the added iodine. In Table III.

some appropriate results are given.

The "Order" of the Reaction, and Influence of Aldehyde Concentration on the Rate.

That the reaction is roughly "of the first order" is apparent from the values of $t_{\frac{1}{2}}$ at different initial pressures; those given in Table IV. are calculated on the basis of the calibration data of Table III.

The course of the reaction as represented by the curves of Fig. 1 is also to a first approximation represented by an expression of the first order, but there is in general a uniform decrease of the

$$\text{constant } k = \frac{1}{t} \log \frac{a}{a-x}$$

throughout any individual run. Typical results at 392° C. in an unpacked

TABLE IV.—TEMPERATURE 392° C. 4 mm. CATALYST. UNPACKED VESSEL.

Initial Pressure, mm.	$t_{\frac{1}{2}}$ Secs.	Initial Pressure, mm.	$t_{\frac{1}{2}}$ Secs.
40	132	262	122
59	115	310	112
71	135	393	126
105	118	464	120
138	118	536	108
192	127	—	—

vessel, using in all cases 4 mm. catalyst, are given in Table V., t is given in secs.

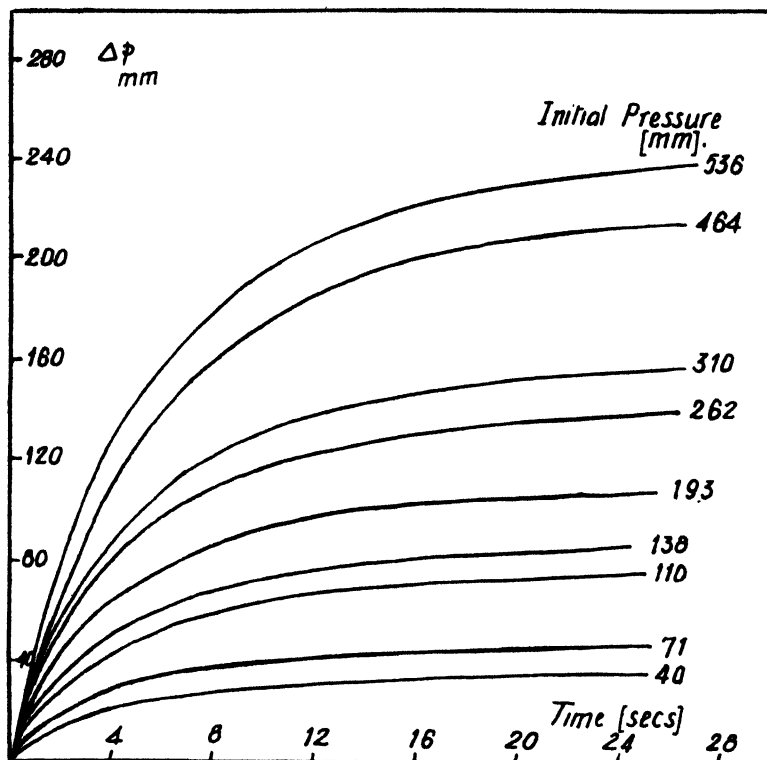


FIG. 1.—Unpacked Vessel.

That the course of the reaction is not simple is also indicated by the values of the ratios $t_1 : t_2$ and $t_2 : t_3$.

A reason for the peculiarities was at first sought in the possibility that

TABLE V.

(1) $p_0 = 40$ mm.; $a = 26$.			(2) $p_0 = 193$ mm.; $a = 99$.			(3) $p_0 = 393$ mm.; $a = 184$.		
t .	x .	$k \times 10^4$.	t .	x .	$k \times 10^4$.	t .	x .	$k \times 10^4$.
30	5	31	19	10	24	12	10	20
70	10	30	44	20	22	25	20	20
148	15	25	73	30	21	45	30	17
238	18	21	115	40	19	65	40	16
450	22	18	170	50	18	88	50	15
640	24	17	307	70	17	125	64	15
1080	25	13	508	84	16	215	94	14
end	26	—	830	93	14	260	104	14
			end	99	—	448	138	13
						695	160	12
						1230	178	12
						end	184	—

the rate of pressure increase is not a true measure of the rate of disappearance of acrolein. An error of this kind cannot however be responsible

TABLE VI.—TEMPERATURE 392° C.
4 mm. CATALYST. UNPACKED
VESSEL.

p_0 mm.	$k' \times 10^4$.
40	33
71	33
172	32
193	25
262	23
310	24
393	20
553	21

for the uniform drift of k , which is still found after the corrections have been made. This might have been expected in any case, since the runs at lower pressures which require no correction show the uniform fall of k over their course.

It appears that acrolein inhibits its own decomposition. If the values of k for any run are extrapolated back to its early stages, a "limiting velocity constant" k' is obtained. The value of k' increases noticeably with decreasing initial pressure.

Moreover, for a fixed catalyst concentration, except at the lowest pressures, the initial rate varies with a

power of the initial pressure much less than the first in value, and approximately 0.5.

An inhibiting effect of this kind has been noticed in the catalysed decomposition of propionic aldehyde (Bairstow and Hinshelwood).¹ It should however imply an increase, not decrease of k during an individual run. Two causes might bring about the observed effect. On the one hand the products of the decomposition might retard the reaction; but separate experiments showed that this effect was slight, if at all observable. A more probable explanation is that iodine is slowly removed during the course of the reaction by the hydrogen and unsaturated products formed.

For this reason accurate values of the initial rate, although perhaps more difficult to measure, are of greater

TABLE VII.—TEMPERATURE 392° C. 4 mm.
CATALYST. UNPACKED VESSEL.

p_0 mm.	Initial Rate mm./min.	$k_{4u}^{392} = \frac{\text{Initial Rate}}{\sqrt{p_0}}$
40	10.0	1.6
59	14.0	1.8
71	15.0	1.8
110	26.0	2.4
153	26.5	2.1
172	30.0	2.3
192	29.0	2.1
262	32.5	2.0
310	35.0	1.9
393	39.0	1.9
464	40.0	1.9
536	47.0	2.0
553	53.0	2.3

TABLE VIII.

Pressure of Acrolein, mm.	$t_{\frac{1}{2}}$	Initial Rate mm./min.	$k_{8p}^{388} = \frac{\text{Initial Rate}}{\sqrt{p_0}}$
322	103	40.0	2.2
103	88	28.0	2.7
149	100	30.0	2.4
446	110	50.0	2.3
208	101	32.5	2.3

service than the periods of half-change in the analysis of the kinetics, since the iodine will disappear in the secondary processes at different rates under the different conditions of pressure and temperature.

In a packed vessel the above relationships were completely reproduced. Table VIII. gives the data at 388° C. with 8 mm. catalyst in each experiment. The mean values of the quotient in column 4 for three different concentrations of catalyst are $k_{2p}^{388} = 1.0$, $k_{4p}^{388} = 1.8$ and $k_{8p}^{388} = 2.4$.

The Influence of Catalyst Concentration on the Velocity of Reaction.

The effect on the reaction velocity of varying the catalyst concentration over the range 0-15 mm. was studied, with higher concentrations subsidiary complications make the study impracticable. Over this range of catalyst concentration the initial rate of reaction is roughly proportional to the square root of the iodine concentration. Table IX. embodies the data of experiments at 388° C. in the unpacked vessel. In all cases the pressure of acrolein was within a few mm. of 20 mm.

TABLE IX.

Pressure of Iodine, mm.	$t_{\frac{1}{2}}$ Secs.	Initial Rate mm./min.	Initial Rate $\sqrt{p_{I_2}}$
0.33	750	6	10.5
1.0	414	10	10.0
1.33	300	14	12.2
2.0	225	18	12.8
3.0	180	24	13.9
4.0	152	30	15.0
5.0	112	36	16.0
6.0	105	39	15.8
8.0	81	45	15.9
10.0	78	48	15.2

In the packed vessel similar conclusions follow. Fig. 2 shows the relationship between initial rate and iodine concentration in this case. At 388° C. using 200 mm.

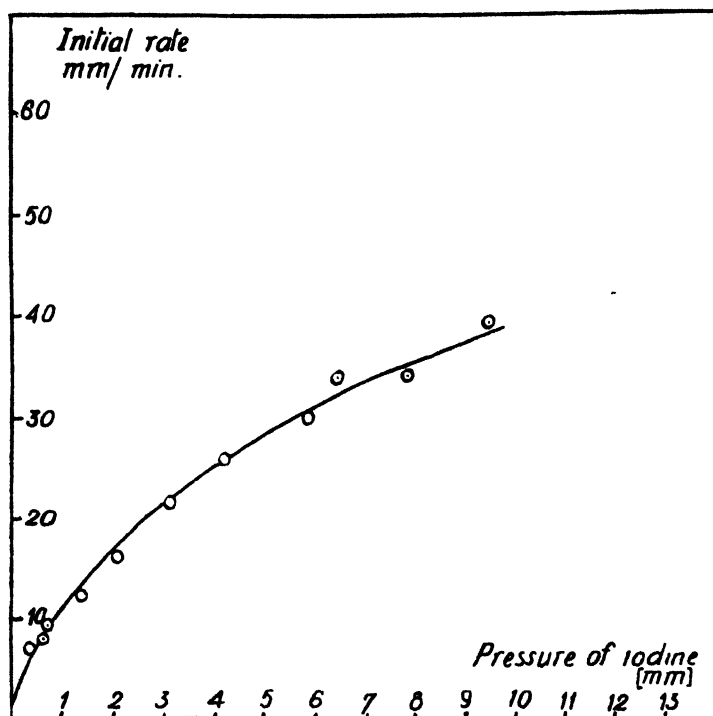


FIG. 2.—Packed Vessel. 388° C. 200 mm. Acrolein.

acrolein in each experiment; the value of the quotient $\frac{\text{initial rate}}{\sqrt{p_{I_2}}}$ ranged from 12-15, the mean being 12.9.

If from the data of Table IX., $\log t_1$ is plotted against $\log p_{I_2}$, a marked straight line is obtained. The regularity may be largely accidental, but in so far as it is significant the slope of -0.6 implies that the rate of reaction varies as $[I_2]^{0.6}$. The results in a packed vessel at 388°C . suggest the relationship, rate $\propto [T]^{0.38}$.

The Homogeneity of the Process.

The marked reproducibility of the process is almost adequate proof of the absence of appreciable surface reaction. Packing of the reaction vessel decreased the "end-point", *i.e.*, there was a smaller percentage pressure increase, at the higher initial pressures. This never exceeded a few per cent. Making corrections for this the course of the reaction was still somewhat different in the two vessels. At 388°C . in an empty vessel the mean value of t_1 for ten different runs using initial pressures 50-450 mm. and 4 mm. catalyst in each case was 140 secs. In a packed vessel but otherwise identical conditions the value was 165 secs. The retardation by packing is also apparent in the values of k' especially at the highest pressures. The retardation cannot be regarded as considerable, and if reaction chains are involved at all, they must be very short.

The Influence of Temperature upon the Velocity of Reaction.

This can be studied in two ways, using either $1/t_1$ or the "initial rate" as a measure of the reaction velocity constant. In consequence of the continuous removal of catalyst as already described however, and the unsatisfactory nature of t_1 , the energy of activation is best deduced by plotting $\log(\text{rate})$ against $1/T$. Table X. gives the relevant data in an empty vessel, the values of t_1 and of the initial rate being in each case corrected so as to correspond to units of concentration 200 mm. acrolein and 4 mm. of iodine at 388°C .

TABLE X.

$^\circ \text{C}$.	t_1 Secs.	Initial Rate mm./min.
358	700	7.3
378	247	17.4
388	145	30.0
398	90	40.1
408	59	54.2
418	38	75.4

The value of E obtained is 32,000 Cals.; using t_1 the value is 40,000 Cals.

In the packed vessel with the same initial concentrations and over the range 368° - 418°C . the corresponding values are 31,300 and 38,200 Cals.; and with halved concentrations of catalyst 30,600 and 38,500. That the lower values (ca. 32,000) are the more significant must again be emphasised, and the results got from t_1 are only given to indicate the order of the discrepancy.

Discussion.

The kinetics of the process described above are complicated and unsuitable for a detailed analysis, but certain conclusions are definite. In the presence of iodine, acrolein vapour decomposes at temperatures more than 100°C . lower than in the absence of the catalyst. There are signs that in the catalysed reaction a "unimolecular" decomposition giving ethylene occurs to a greater extent than in the uncatalysed process. The acrolein appears to have the power of retarding its own decomposition, presumably by some type of chain breaking process. The effect of vessel dimensions shows that reaction chains, if present, must however be short.

The velocity of reaction is approximately proportional to the square root of the concentration of iodine. It is impossible without further

knowledge to decide whether this implies catalysis by iodine atoms rather than by iodine molecules, since a simultaneous positive and negative catalytic effect of the iodine would equally well explain the facts. The catalysed process has a lower energy of activation (ca. 32,000 Cals.) than the uncatalysed decomposition (ca. 38,000 Cals.).

Calculations on the molecular statistics must in the circumstances be tentative, but they appear to suggest catalysis by molecular iodine. At 388° C. with 200 mm. acrolein and 2 mm. iodine, it can be shown from the above data that the number of molecules of acrolein reacting per c.c. per sec. is 8.9×10^{15} . Taking the molecular diameters of the iodine and acrolein molecules to be respectively 4×10^{-8} and 5×10^{-8} , the number of collisions per c.c. per sec. at this temperature and with

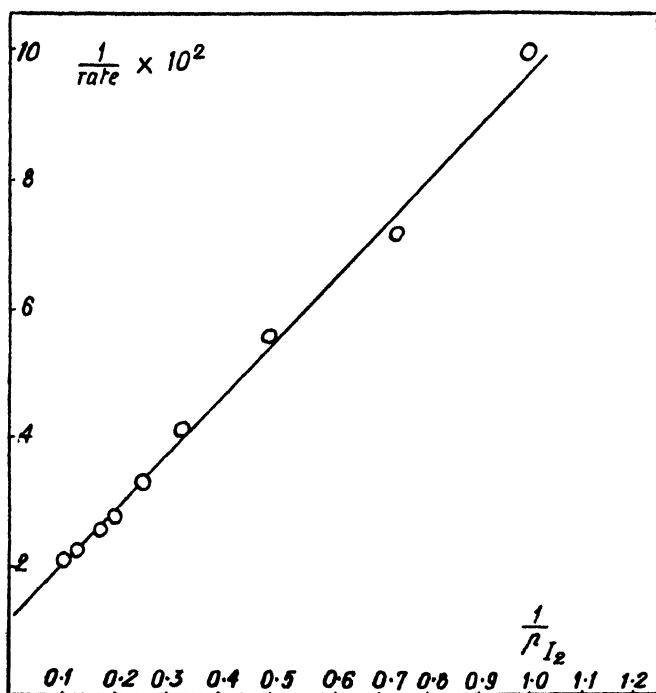


FIG. 3.—Rate expressed in mm./min. Iodine pressure expressed in mm.

these concentrations between acrolein and iodine molecules is 1.7×10^{25} . Assuming an energy of activation of 32,000 Cals. and the operation of two squared terms, this gives 4×10^{14} "activated" collisions per c.c. per sec. The higher and probably incorrect energy of activation of 39,000 Cals. gives 1.9×10^{15} . In the former case the observed rate is therefore some twenty-fold greater than that calculated.

From the data of Bodenstein and Stark³ it can be shown that at 2 mm. and 388° C. the number of iodine atoms per c.c. is ca. 5×10^{14} . Assuming an iodine atomic diameter of 3×10^{-8} the number of collisions per c.c. per sec. between acrolein molecules and iodine atoms under the same conditions as above is 3×10^{23} . Allowing for the energy of dissociation of the iodine molecule, this will now have to be multiplied

³ Z. Elektrochemie, 1910, 16, 966.

by the factor $e^{-14,000/RT}$, giving a number of "activated" collisions 6.6×10^{18} . The higher energy of activation gives 3×10^{18} . It is seen that the measured rate is much lower than these.

On the whole therefore it seems probable that the catalysis occurs via iodine molecules, the propagation and breakage of short chains accounting for the outstanding facts. Assuming both propagation and breakage of chains by both the iodine molecule and the acrolein, the general expression for the reaction rate will be of the form

$$\frac{k_1 F'(c_{\text{acrolein}}) F'''(c_{\text{iodine}})}{k_2 + k_3 F'(c_{\text{acrolein}}) + k_4 F'''(c_{\text{iodine}})},$$

or for a constant initial concentration of acrolein the rate will be given by

$$\frac{K' [I_2]}{K'' + K''' [I_2]} \quad \text{so that} \quad \frac{1}{\text{rate}} = a + \frac{b}{[I_2]}.$$

Plotting $\frac{1}{\text{rate}}$ against $\frac{1}{[I_2]}$, a straight line should be obtained, cutting the axis with a small positive intercept. The latter will imply a limiting maximum catalytic effect of the iodine. If the data of Table IX. are considered from this standpoint, omitting the experiment with 0.33 mm. catalyst, where small errors are greatly magnified, agreement is found as shown by Fig. 3.

Summary.

The homogeneous catalysis of the decomposition of acrolein by iodine has been studied. Under these conditions the reaction occurs some 100° C. lower than in the absence of catalyst. The velocity of reaction is roughly proportional to the square root of the concentration of catalyst, but this does not necessarily imply catalysis via iodine atoms rather than iodine molecules. The acrolein itself appears to retard its own decomposition. The complexity of the process makes detailed considerations on the molecular statistics profitless.

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A LABORATORY STUDY OF THE ATMOSPHERIC CORROSION OF METALS.

Part II.—Iron : The Primary Oxide Film.

Part III.—The Secondary Product or Rust (Influence of Sulphur Dioxide, Carbon Dioxide, and Suspended Particles on the Rusting of Iron).

BY W. H. J. VERNON.

Received 15th October, 1935.

General Introduction.

The previous communication ¹ in this series dealt with the behaviour of copper on exposure to various synthetic atmospheres, and in this and accompanying papers ² the technique employed in the experiments was

¹ (a) *Trans. Faraday Soc.*, 1931, **27**, 255; (b) *ibid.*, 582.

² *Ibid.*, 241 and 248.

described. Since that time work of a more specific nature—e.g., the investigation of the "fogging" of nickel,³ and the further study of the green patina on copper and its reproduction artificially⁴—has been reported; but attention has meanwhile been directed toward the atmospheric corrosion of iron, and it is with this part of the work that the two present communications are concerned.

Several of the lines of inquiry arose out of the author's First and Second Reports to the Atmospheric Corrosion Research Committee (British Non-ferrous Metals Research Association).⁵ In this earlier work, for example, it was found that the rusting of iron in air, out of contact with rain, is not necessarily associated with the meteorological dewpoint, as usually supposed; a profound increase in the rate of attack was identified with a critical humidity very considerably below saturation. Rusting could be suppressed entirely by screening the specimen within a muslin "cage" or by filtering the air so that contact with suspended solid particles in the atmosphere was avoided. Furthermore, iron specimens exposed to screened or filtered air developed an invisible film (presumed to be oxide) the protective effect of which could be demonstrated by subsequent normal exposure with freshly-cleaned comparison specimens.

In a recent paper⁶ in which the position immediately prior to the present experiments was surveyed, the study of the atmospheric corrosion of iron was regarded as comprising both the primary (normally invisible) oxide film and the secondary product or rust. The present series of experiments has been approached from this point of view, and the results are accordingly reported in two papers, dealing with the primary film and the secondary rust respectively.

Metal Used in Experiments.—A "datum" material was sought, of reasonably high purity and ready reproducibility, that would be directly comparable with other grades of iron and steel in common industrial use. Such a material was secured⁷ in a mild steel sheet of "deep stamping quality," the analysis of which is given below. Most of the experiments were carried out with steel "G," but in others steel "T" (supplied at a later stage) was used; experiments designed with the object of checking the agreement yielded by the two steels, within the range of conditions covered by the present two papers, have given exceedingly satisfactory results.

Mark.	C.	Si.	Mn.	S.	P.	Cu.
G.	0.12	0.01	0.39	0.052	0.029	0.12 per cent.
T.	0.081	0.01	0.39	0.040	0.035	0.10 "

The sheets "as rolled" had Diamond Pyramid hardness numbers ranging from 152 to 166, but in the main experiments annealed sheet (hardness numbers 75 to 92) was used.

Specimens.—The specimens were similar in dimensions to the copper specimens of the previous series (5.0 × 5.0 cm. accurately) but slightly thicker (0.75 mm. approx.; average weight of specimen, 15 grams). Preliminary treatment of the sheet for removal of scale was carried out industrially by abrasion with emery of successively diminishing fineness;

³ *J. Inst. Metals*, 1932, 48, 121.

⁴ (a) *Ibid.*, 49, 153; (b) *ibid.*, 1933, 52, 93; (c) *J. Chem. Soc.*, 1934, 1853.

⁵ (a) *Trans. Faraday Soc.*, 1924, 19, 886; (b) *ibid.*, 1927, 23, 159.

⁶ Vernon, *Trans. Electrochem. Soc.*, 1933, 64, 31.

⁷ Cordial thanks are tendered to Messrs. Glynhir Tinplate Co., Pontardulais, for the supply, through the courtesy of Mr. O. J. Thomas, of the mild steel sheet used throughout the work (Parts II. and III.).

the final preparation by Hubert No. 1 emery paper was applied in the laboratory to the separate specimens immediately prior to each experiment. Degreasing was effected in a bath of pure benzene, followed by two baths of pure carbon tetrachloride.

Weighing of the specimens was conducted according to the Conrady system⁸ used in the previous work.

Part II.—Iron : The Primary Oxide Film.

Much work has been done on the high-temperature oxidation of iron, *e.g.*, Pilling and Bedworth,⁹ Pfeil,¹⁰ Portevin, Pretet and Jolivet;¹¹ the coloured films produced at intermediate temperatures have been studied by T. Turner,¹² and much more recently by Tammann, Mallock, Gale, U. R. Evans and others;¹³ certain properties of the invisible film formed at ordinary temperatures were reported by the present author,¹⁴ whilst optical methods for its examination have been employed by Freundlich, Patscheke, and Zocher,¹⁵ and by Tronstad.¹⁶ Further information appeared, however, to be needed before the properties of the invisible film could be correlated with those produced at the higher temperatures; and it was with the object of obtaining some such information that the present experiments were instituted.

Experiments with a similar object have already been carried out by the present author in the case of copper.¹⁷ Here a minimum thickness of the oxide film was observed (produced by an hour's heating at 75°) at which protection against atmospheric tarnishing commenced; assuming a real surface area twice that of the nominal area (see p. 1673) this thickness, from gravimetric evidence, was approximately 5 Å. (*cf.* lattice dimension of cuprous oxide, 4.28 Å.). Beyond this point, however, no further change in the properties of the oxide film was observed for temperatures of heating extending up to 250°. For any given temperature a parabolic relationship between film thickness and time was closely followed. The relation between temperature and rate of oxidation was found to conform to the equation (identical in form with the empirical equation of Arrhenius) developed by Dunn¹⁸ from quantum principles for the special case of the rate of metallic oxidation, as follows—

$$d \log W/dT = - Q/RT^2.$$

The persistence of this relationship for temperatures from 300° to 600° has since been shown by Hudson, Herbert, Ball, and Bucknall,¹⁹ the curves obtained in the two researches being identical in slope and very nearly continuous.

⁸ A. E. Conrady, *Proc. Roy. Soc.*, 1922, 101A, 211. See also W. H. J. Vernon, *J. Soc. Chem. Ind.*, 1934, 53, 211.

⁹ *J. Inst. Metals*, 1923, 29, 529.

¹⁰ *J. Iron Steel Inst.*, 1931, 123, 248.

¹¹ *Rev. Met.*, 1934, 31, 101, 186, 219. (Other references to cognate literature, particularly "scaling" in furnace atmospheres, are incorporated in these papers.)

¹² *Proc. Birm. Phil. Soc.*, 1889, 6, 296.

¹³ See U. R. Evans, *Proc. Roy. Soc.*, 1925, 107A, 228.

¹⁴ *Trans. Faraday Soc.*, 1927, 13, 159.

¹⁵ *Z. physikal. Chem.*, 1927, 128, 321; 130, 289.

¹⁶ *Ibid.*, 1934, 170, 172.

¹⁷ *J. Chem. Soc.*, 1926, 2273.

¹⁸ *Proc. Roy. Soc.*, 1926, 111A, 203.

¹⁹ *J. Inst. Metals*, 1929, 42, 243.

Experimental.

The experimental method was simple and consisted in heating the specimens in air at known temperatures and determining the increase in weight resulting from film formation. The more critical experiments were

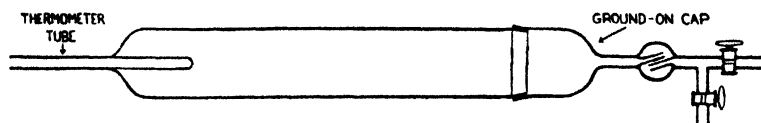


FIG. 1.—Apparatus used in oxidation experiments.

carried out in purified and desiccated air, using the apparatus illustrated in Fig. 1.²⁰ This consists of a hard glass tube, 8 cm. int. diam., fitted with a ground-on cap and side-tube with stop-cocks for the purpose of evacuation and filling. At one end a tube closed at its inner end projects into the main vessel and carries a thermometer. The middle portion of the apparatus is surrounded by an electrically-heated tube furnace, the temperature being regulated by hand-controlled rheostats. Before commencing any experiment, a considerable time was allowed for the temperature to become constant; and the results would seem to show that no appreciable vitiation occurred through lack of automatic temperature control. The specimen was supported on a glass frame (Fig. 1A) constructed of glass rod and giving a minimum of contact.

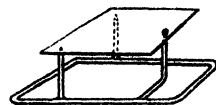


FIG. 1A.—Method of supporting specimen.

In order to save time, other experiments using the same method of suspending specimens, were carried out in an ordinary electrically-heated

TABLE I.—EXAMPLES OF WEIGHT-INCREMENTS.

Milligrams (Actual). Total Area of Specimen = 0.5 Sq. Decim.

Purified Air. 25° (10 Per Cent. Relative Humidity).

Time in Days.	Expt. 148. No. Mgm.	Expt. 149. No. Mgm.	Time in Days.	Expt. 148. No. Mgm.	Expt. 149. No. Mgm.	Time in Days.	Expt. 148. No. Mgm.	Expt. 149. No. Mgm.
1	122 0.006 124 0.005	134 0.011 135 0.002 136 0.007 137 0.005	15	122 0.051 124 0.042	134 0.043 135 0.037 136 0.045 137 0.046	35	122 0.067 124 0.059	134 0.071 135 0.064 136 0.068 137 0.064
4	123 0.015 125 0.010	134 0.017 135 0.008 136 0.015 137 0.012	20	123 0.051 125 0.045	134 0.049 135 0.045 136 0.053 137 0.054	40	123 0.078 125 0.070	134 0.079 135 0.072 136 0.077 137 0.076
7	122 0.023 124 0.021	134 0.026 135 0.014 136 0.022 137 0.024	25	122 0.058 124 0.056	134 0.058 135 0.050 136 0.062 137 0.058	50	123 0.085 125 0.085	134 0.088 135 0.085 136 0.088 137 0.084
11*	123 0.035 125 0.025	134 0.035 135 0.028	30	123 0.063 125 0.054	134 0.065 135 0.060 136 0.062 137 0.060			
12†		136 0.031 137 0.034						

* Expt. 148.

† Expt. 149.

²⁰ The experiments at 25° were carried out in the air thermostat (see Part III. and previous work).

1672 STUDY OF ATMOSPHERIC CORROSION OF METALS

muffle furnace that had been used for no other purpose than heating clean metal specimens; hence there was no contamination arising from the furnace itself, whilst the air admitted to the furnace, although not purified, was particularly free from impurities. Results from parallel experiments under the two conditions, gave no appreciable difference, within experimental error (see examples in Table II. for temperatures of 50°, 100° and 200°).

TABLE II.—EXAMPLES OF WEIGHT-INCREMENTS.

Milligrams (Actual). Total Area of Specimen = 0.5 Sq. Decim.

50° and Higher Temperatures.

Time (Hours). 50°	Mgm.	Time (Hours). 175°	Mgm.	Time (Hours). 195°	Mgm.
8	0.013	19	0.122	91	0.382
16	0.020	20	0.132	"	0.352
23	0.023	44	0.191		
24	0.025	91	0.251	200°	
43	0.033	"	0.253	1	0.054
65	0.043—Purified	231	0.320	3	0.096
72	0.046 } [Air	"	0.320	"	0.099
91	0.054			"	0.095 } Purified
160	0.066 } Purified	185°		19	0.242 } Air
167	0.068 } Air	3	0.078	"	0.233
		"	0.077	"	0.248
100°		21	0.167	"	0.238
6	0.031	"	0.163	90	0.529
18	0.052	45	0.223	"	0.525
24	0.061	"	0.208		
44	0.095	192	0.342	225°	
45	0.085			1	0.087
"	0.089	190°		3	0.149
115	0.137 } Purified	3	0.084	15	0.332
"	0.124 } Air	"	0.082	"	0.339
186	0.162	22	0.178	40	0.540
"	0.144	"	0.192	"	0.543
		42	0.227	65	0.690
175°		"	0.215	"	0.696
1	0.037	96	0.289		
"	0.036			250°	
3	0.067	195°		1	0.142
"	0.064	3	0.090	"	0.131
"	0.068	"	0.089	3	0.226
"	0.065	19	0.213	6	0.314
8	0.091	"	0.210	"	0.327
"	0.089	69	0.342	91	1.287
19	0.126	"	0.332	"	1.215

Results and Discussion.

Oxidation/Temperature Relationships.—Agreement with the Dunn equation requires a linear relationship between the logarithm of the reaction rate and the reciprocal of the absolute temperature. In Fig. 2 logarithms of weight-increments for one hour's heating are plotted against reciprocals of absolute temperature. For temperatures of 130° upwards the values plotted were directly determined; for lower temperatures, except 25°, they were obtained by interpolation from the oxidation/time curves (the earliest determined values for 100°, 50° and 25° occurred at 6, 8 and 24 hours). The interpolated value for 25° falls very considerably below

the straight line given by the other temperatures; this apparent anomaly, and the derivation of the value actually plotted, is discussed later.

The striking feature of Fig. 2 is the point of inflection at 200° , above and below which agreement with the equation is indicated, with a change in the constants at the critical point, denoting some change in the properties of the oxide film at that temperature. The validity of this transformation has been confirmed by several lines of evidence, as follows:—

Visual Evidence.—The operation of steel tempering makes use of the sequence of interference ("temper") colours produced at temperatures above 200° ; but it is commonly understood²¹ that the colours may be produced at lower temperatures if the heating is sufficiently prolonged. In the present experiments the development of interference colours has been found to depend in a very striking manner upon whether the heating is conducted above or below the critical temperature of 200° . Above this temperature they may be produced and reproduced with the greatest precision: thus, any given colour can be obtained at alternative temperatures, the appropriate times being given by calculation from the corresponding parabolas (*vide infra*). For example, the characteristic blue (weight-increment 0.66 mg./dm.^2) is given by heating for 15 hours at 225° , 6 hours at 250° , 1.25 hours at 275° , or 7 minutes at 350° . Assuming the film to consist of Fe_2O_3 (*vide infra*) of density 5.25, then if the real area of the specimen is known, a simple calculation gives the thickness of the film. In the earlier work on copper,⁷ the real area of the emiered surface was assumed to be approximately twice that of the nominal area. Recent work by Erbacher²² on the determination of the absolute surface area of

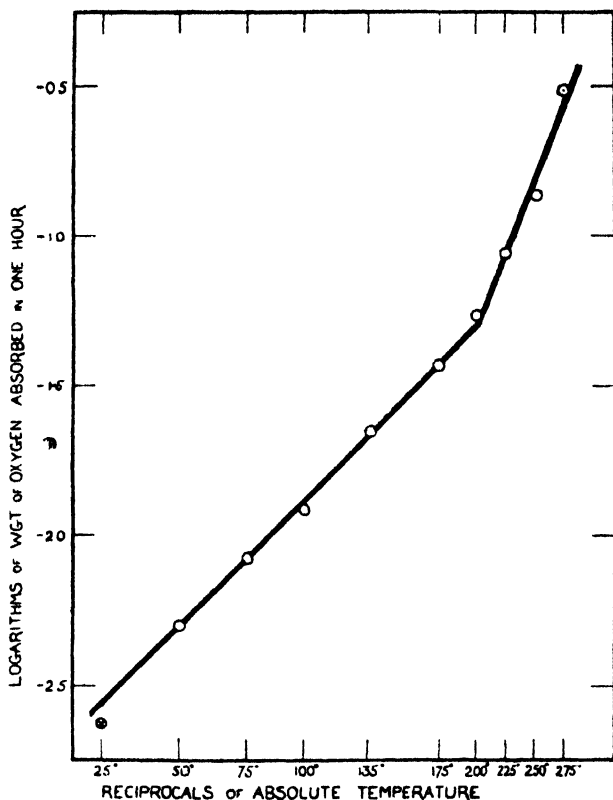


FIG. 2.—Relation between temperature and rate of oxidation.

blue (weight-increment 0.66 mg./dm.^2) is given by heating for 15 hours at 225° , 6 hours at 250° , 1.25 hours at 275° , or 7 minutes at 350° . Assuming the film to consist of Fe_2O_3 (*vide infra*) of density 5.25, then if the real area of the specimen is known, a simple calculation gives the thickness of the film. In the earlier work on copper,⁷ the real area of the emiered surface was assumed to be approximately twice that of the nominal area. Recent work by Erbacher²² on the determination of the absolute surface area of

²¹ Turner¹⁸ was apparently the earliest to attempt to show this experimentally.

²² *Z. physikal. Chem.*, 1933, 163, 215. The determination of absolute surface area has already been studied by Bowden and Rideal, *Proc. Roy. Soc.*, 1928, 120A, 59, 80; and by Bowden and O'Conner, *ibid.*, 1930, 128A, 317.

metals (using a method that depends on the quantity of more noble atoms deposited in a monatomic film on the metal surface) has shown that by rubbing with emery paper, independent of its fineness, the surface is increased 2.5 times. Employing this value, the thickness of the film which gives the first blue interference colour is given as 1.68×10^{-6} cm., i.e., 168 Å. Similarly, the orange interference colour corresponds to a thickness of 56 Å.

At temperatures below 200° , however, this simple relationship no longer obtains, and interference colours do not appear even though the thickness of the film, as given by weight-increment, is considerably greater than that which, above the critical temperature, would give the characteristic colours. At 135° and lower temperatures the films were "invisible" at all periods of exposure.²² At 175° 230 hours heating gave a weight-increment of 0.65 mg./dm.², but no colour beyond a pale brown, the general effect being a gradual darkening. On the other hand, at 225° , 3 hours heating gave a bright bluish-purple colour with a weight-increment of only 0.30 mg./dm.². Traces of colour may be obtained by prolonged heating at temperatures not much below 200° , but these, besides being

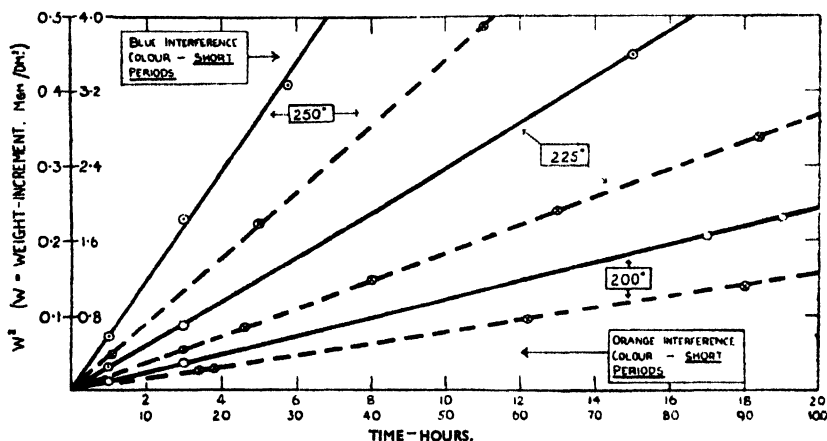


FIG. 3.—Relation between film thickness (weight-increment) and time (W^2/T) at 200° and higher temperatures.

(Broken curves are "long periods.")

"dirty" and ill-defined (in contrast with the bright colours produced above 200°), are not such as would be predicted on the interference view. Thus, at 195° the first colour to appear was a trace of purple at 69 hours (weight-increment 0.66 mg./dm.²), and at 185° a trace of mauve at 192 hours (0.68 mg./dm.²). It is clear, therefore, that the film below 200° has properties essentially different from that produced above 200° . The effect upon light is no longer that of refraction in a transparent continuous envelope; it would seem to be rather a diffraction effect at the air interface of a relatively thick film which, near the surface at least, has a granular structure. Even at 25° , not unduly long periods of exposure are required to produce ("invisible") films comparable in thickness with the coloured films above 200° . Thus, at 65 days and 600 days the films at 25° correspond in weight-increment with the orange and blue films respectively above 200° . Evidently, therefore, except above the critical temperature of 200° , colour is not a simple function of film thickness.

²² The change in appearance of a single specimen on prolonged exposure at the lower temperatures is not immediately obvious to the eye, and films so produced are conveniently described as "invisible"; nevertheless, a darker appearance is usually discernible when comparison is made with a freshly cleaned specimen.

Oxidation/Time Relationships.—In Figs. 3 and 4 squares of weight-increments are plotted against time of heating. At temperatures including and above 200° (Fig. 3) the straight lines show close agreement with the parabolic law, and the process is therefore controlled by simple diffusion through a continuous homogeneous film, *i.e.*,

$$\frac{dw}{dT} = \frac{k}{w}, \quad \text{or} \quad w^2 = Kt.$$

On the other hand, temperatures below 200° (Fig. 4) are distinguished by a marked departure from the parabola, the quadratic curves flattening toward the time axis. The deviation is apparently the more marked the higher the temperature, short of 200° when a sharply defined reversion to the parabola occurs.

In all the examples in Fig. 4, sufficiently close agreement with the parabola is exhibited in the *very early stages* to justify interpolation to one

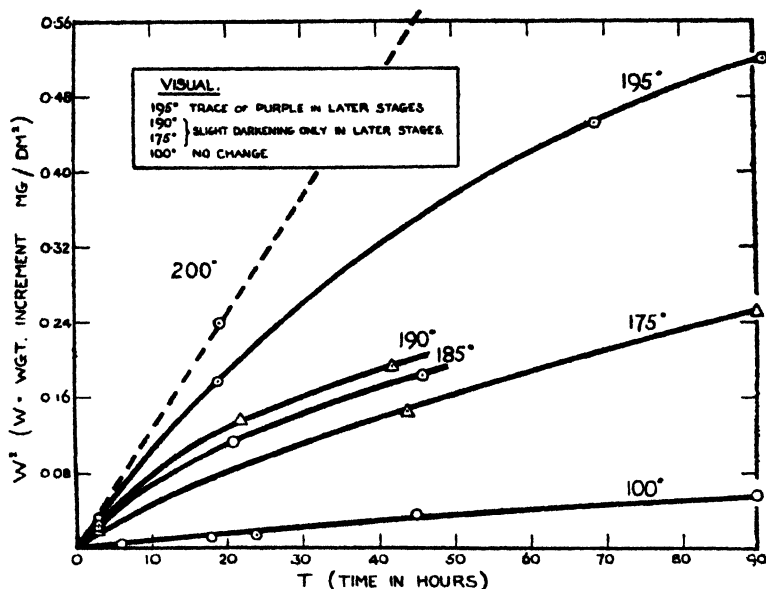


FIG. 4.—Relation between film thickness (weight-increment) and time (W^2/T) at temperatures below 200° .

hour. At 50° (not shown in figure) there is a very slight departure during the first 90 hours, but this takes the form of a concavity about the vertical axis as distinct from the convexity that develops later; the effect on the interpolated value at one hour (assuming a parabolic relationship) is, however, negligible. At 25° , on the other hand, the initial concavity which persists up to 15 days, is much more marked. As the interpretation of this phenomenon is important, the evidence is shown in Fig. 5, where both weight-increments and squares of weight-increments are plotted against time. The early part of the quadratic curve (inset on a more open scale) shows clearly the initial concavity, with a sharp point of inflection at 15 days when a strictly parabolic relationship is assumed. At 35 days there is another point of inflection, and from this point an "approximate parabola" is followed; the deviation is in the same direction as at the higher temperatures, the curve tending to flatten toward the time axis.

Considering the first point of inflection, this occurs at a weight-increment of 0.082 mg./dm.^2 , which, on the same basis of calculation as before,

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corresponds with a film of 20.8 \AA , *i.e.*, approximately $2\frac{1}{2}$ times the unit cell thickness of $\gamma \text{ Fe}_2\text{O}_3$. Except as indicating the order of magnitude of thickness, significance is not attached to these derived values in the absence of information as to the composition and structure of the film, for both of which several alternatives are possible. Nevertheless, the point of inflection is too well marked and reproducible to be fortuitous; the explanation suggested is that it coincides with the completion of the unit lattice of the oxide over the whole surface of the specimen. Oxidation would be expected to occur more readily at the edges, at the suspension hole, and at the ridges of scratches; thus, by the time unit cell thickness is completed over

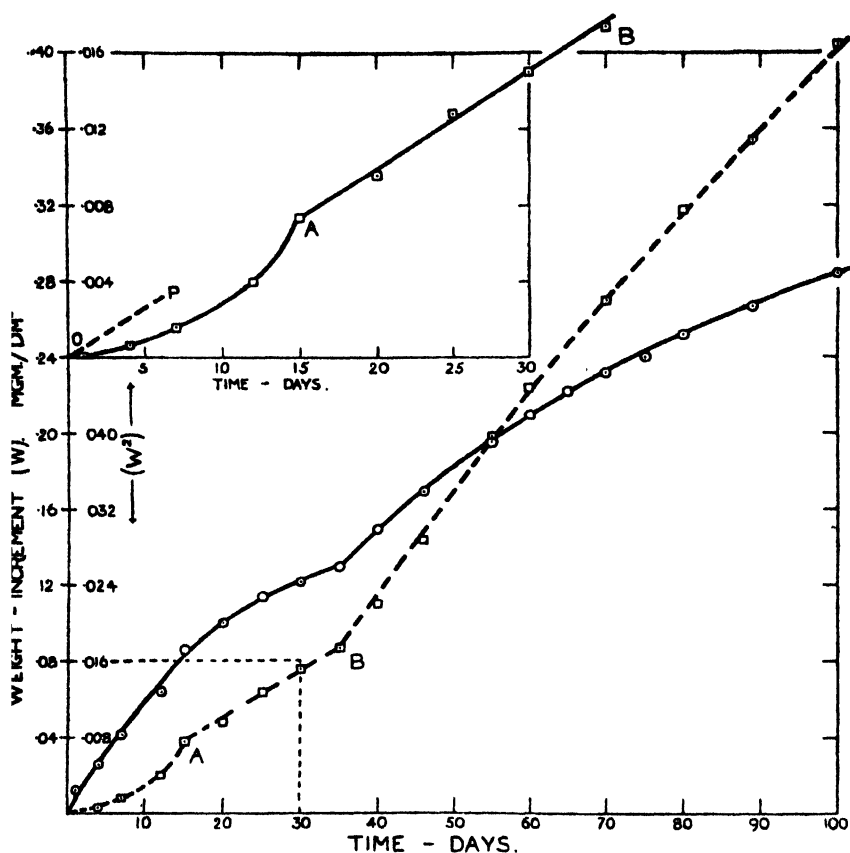


FIG. 5.—Relation between film thickness (weight increment) and time. 25°C . Broken curve and inset curve are "squares" (W^2/T).

the less reactive places, a considerably greater thickness may be reached at the "high spots." When once completed for the whole surface, however, further attack on the metal can take place only by diffusion of oxygen through the first formed lattice; hence the parabolic relationship beyond the point of inflection. The interpretation of the different rate of attack up to this point is that it marks the building up of the primary oxide lattice, a process that is clearly not so rapid as commonly supposed. An explanation of the apparent anomaly exhibited by the value for 25° on the oxidation/temperature curve is now forthcoming. At the higher temperatures the whole surface is covered with a completed oxide lattice well within the hour—the arbitrary time chosen for the values plotted in Fig. 2;

but at 25° this process is very far from being completed in one hour, and hence the value derived from the real weight-increment is too low to fall on the curve.²⁴ If, however, in Fig. 5, a line be drawn through the origin (see OP, inset) parallel with the (quadratic) straight line immediately after the point of inflection, then the interpolated weight-increment for one hour²⁵ is in satisfactory agreement (having regard to the smallness of the magnitudes involved) with the temperature/oxidation curve (see plotted value for 25°, Fig. 2). The interpretation of the hypothetical values yielded by OP (Fig. 5) is that they represent values that would be realised *if a parabolic relationship with time obtained from the start* instead of only when the unit lattice is completed.

The second point of inflection is explained as follows. In the light of Finch and Quarrell's work on zinc,²⁶ the first formed oxide is probably pseudomorphic with iron; when unit cell dimensions have been completed, further thickening proceeds by diffusion through the lattice, but it is necessarily accompanied by increasing metastability. At the point of inflection a partial breakdown of the film occurs, with the production of an outer layer composed of the detritus of the primary film; this partial breakdown is naturally accompanied by a temporary increase in the rate of attack. The outer layer is probably made up of granules having the normal structure of Fe_3O_4 , and diffusion is intergranular. The film as a whole is thus duplex in structure and probably continues so as thickening proceeds, the outer layer constituting an increasingly large proportion of the whole. Growth is propagated by the alternate or possibly simultaneous thickening (below) and breakdown (above) of the pseudomorphic film.

On this view the subsequent course of the oxidation/time curve depends on the closeness or otherwise of the packing of the granules in the secondary film. If the packing is very open, so that the resistance to intergranular diffusion is very small compared with the resistance to lattice diffusion in the primary film, then the rate of oxidation is controlled by the primary film; since on hypothesis this remains approximately constant in thickness (probably varying only within molecular limits), it follows that the rate of oxidation will also be constant. This state of affairs is realised in the case of zinc.²⁷ In the present case, however, the falling off in the oxidation rate shows that the resistance of the secondary film must soon become greater than that of the primary film, *i.e.*, the packing must be sufficiently close to impose appreciable resistance to intergranular diffusion. It follows that the depression in the rate of attack must be greater than that which obtains for simple lattice diffusion even in a film of increasing thickness, *i.e.*, the restraining influence of the film must bear an increasingly greater ratio to its thickness. For this reason the oxidation/time curve is depressed toward the time axis to a greater extent than is demanded by the quadratic parabola. Hence the equation

$$W^{2.6} = Kt,$$

which has been found to fit approximately the experimental data for 25° and for other temperatures below 200°.

Electron Diffraction Evidence.—In view of the foregoing evidence concerning the transition temperature at 200°, with changes in properties of the oxide film, an examination of the film by electron camera methods appeared to be highly desirable. At the request of the author, an electron diffraction examination of certain of the films was very kindly undertaken by Mr. G. D. Preston and Dr. L. L. Bircumshaw of the Metallurgy Depart-

²⁴ Interpolated value for weight-increment at one hour = 0.00025 mg. (0.0005 mg./dm.²). $\log W = -3.60$, a value well below the lower limit of Fig. 2.

²⁵ $W = 0.00232$ mg. (0.00464 mg./dm.²). $\log W = -2.63$.

²⁶ *Proc. Phys. Soc. (Lond.)*, 1934, 46, 148.

²⁷ Vernon, *Trans. Faraday Soc.*, 1924, 19, 1863; 1927, 23, 135. See also Tronstad and Höverstad, *ibid.*, 1934, 30, 1122.

ment, N.P.L., through the courtesy of the Superintendent, Dr. C. H. Desch, F.R.S. The examination was somewhat handicapped by the fact that the specimens for the electron camera had to be cut from the larger specimens after use in the oxidation experiments, with consequent risk of spoiling the surface with grease or by mechanical deformation; especially prepared test pieces having a smoother surface would have been more suitable. Nevertheless, the results of this preliminary examination served to reveal a difference in structure between films formed above and below 200°. The diffraction spectra obtained from specimens oxidised at 135° and 175° consisted of rings which corresponded with a cubic structure of side 8.4 Å. This may be either γ -Fe₃O₄ or Fe₂O₃ (the units of these two oxides are identical in size, the former containing twelve molecules and the latter eight). At the higher temperatures new rings made their appearance which were ascribed to rhombohedral α -Fe₂O₃; there was also evidence that, as distinct from films at the lower temperatures, the crystals are oriented on the surface, probably with a (211) plane parallel to the metal.

Part III.—The Secondary Product or Rust (the Influence of Sulphur Dioxide, Carbon Dioxide, and Suspended Particles on the Rusting of Iron).

Introduction.

Experimental.—The procedure in respect to suspension of specimens, manipulation of bell-jars and accessories, purification of air, humidification, air-thermostat, etc., was precisely as in the earlier experiments.⁽¹⁾⁽²⁾ The bell-jars had an average capacity of 10,000 c.c., and normally four specimens were exposed in each. The controlled temperature in the main experiments was 25° C.

Plotting of Results.—In most cases it has been possible to weigh the specimens without any loss of adhering rust; this has permitted the action to be followed from the very early stages by measurement of the increase in weight. Normally, the specimens have been weighed in pairs, taken alternatively from the usual set of four, and the mean weight-increment obtained.

Every curve has been checked by duplicate experiments, typical examples of which are shown in Tables III. and IV.; complete tables of results are omitted through consideration of space. When the time-intervals of the duplicate experiments have been coincident, the means of the two sets of values have usually been plotted; in other cases the values plotted include those from the separate experiments. Since each specimen has a total area of 0.5 sq. dm., the weight increment actually determined is half the plotted value (mg./dm.²) throughout.

RUSTING OF IRON IN PURIFIED AIR.

Unsaturated Atmospheres.

The results show that the rusting of iron in highly pure air is scarcely a serious problem; almost certainly the rusting that gives trouble in service is always associated with impurities in the atmosphere, either gaseous or solid. At 99 per cent. relative humidity the rate of attack (Fig. 6, Curve A) is approximately linear for the first forty days; there is then a marked diminution in the rate, which continues to fall off slightly with time. Corrosion takes the form of isolated rust-spots (characteristic of the atmospheric rusting of iron) of the usual reddish-brown colour, but these are very sparsely distributed. Except at the edges of the specimen, which are always attacked relatively heavily, there is a strong tendency for

rusting to continue at the points of initial attack, and for new centres to start with difficulty (presumably on account of the strengthening of the primary film); for example, at forty days the greater part of the specimen is still bright.

At 50 per cent. relative humidity there is no visible change after prolonged exposure; there is, however, appreciable thickening of the primary invisible film, as shown by the gravimetric changes discussed in Part II.

An interesting state of affairs is revealed in Curve B, Fig. 6. Here the relative humidity, instead of being maintained at 99 per cent. from the start as in A, has been increased in steps (see horizontal scale) from an initial humidity of zero to a maximum of 99 per cent. at thirty-six days, at which value it was maintained for the rest of the experiment. Very slight traces of rust first appeared on the specimen at twenty-four days, following the highest humidity then reached of 70 per cent. (Although the effect is here only very feebly developed, this no doubt corresponds to the critical humidity which, on a much more pronounced scale, is characteristic of the more severe types of rusting to be discussed later.) The rate of

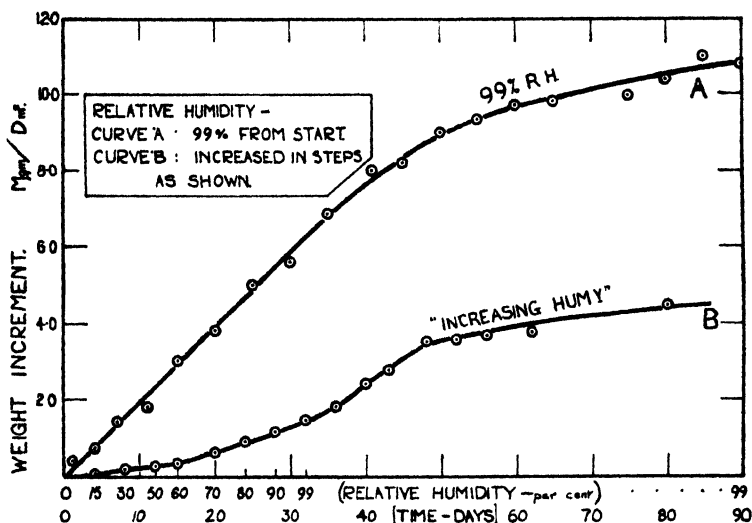


FIG. 6.—Rusting of iron in purified air (constant and "increasing" relative humidity).

attack then increased slightly until about forty days, when a retardation commenced. The significant feature is the very considerable suppression of corrosion as compared with the constant humidity conditions. Even at eighty days rust-spots occupied an estimated area of only 1 or 2 per cent., the rest of the specimen remaining bright; furthermore, considering the latter parts of the curves in Fig. 6, Curve B has a corrosion value approximately only half that of A. This result is most readily explained by the strengthening of the primary film during the period before the critical humidity is reached.²⁸

"Supersaturated" Atmospheres.

Experiments were also carried out under "supersaturated" conditions—i.e., the atmosphere, saturated at the outset, was maintained in contact with water at fluctuating (room) temperature (see p. 1685). Water

²⁸ The absence of carbon dioxide from these experiments must be noted. It is shown later than the normal content of carbon dioxide considerably depresses both curves in Fig. 6, without appreciably affecting their mutual relationship.

condensed freely on the walls of the vessel, and although the specimens were not visibly wet, there can be little doubt that a moisture film must have been present over the whole surface. A characteristic feature of the time-corrosion curves (Fig. 20, Curve B) is that over the first part they are concave about the vertical (corrosion) axis; later, at about seventy days, an approximately linear relationship is assumed. The initial concavity confirms earlier results²⁰, whilst the curve as a whole is strikingly similar (bearing in mind the "uncontrolled" conditions of experiment in each case) to results of Patterson,²⁰ who showed, for supersaturated conditions, an initial concavity changing to linearity at very nearly the same period of exposure as in the present experiments. The first part of the curve contrasts with results for experiments just below saturation (99 per cent. R.H., Curve A, Fig. 6) where, over a similar period, the curve is either linear or concave about the horizontal axis. Thus, in the early stages (up to thirty days in examples quoted) corrosion is actually less

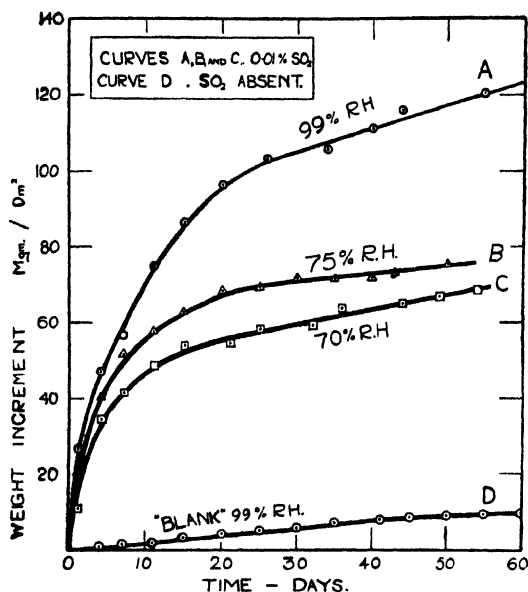


FIG. 7.—Influence of sulphur dioxide at high relative humidity.

under conditions of supersaturation than it is in the unsaturated atmosphere. But whereas under unsaturated conditions strengthening of the primary film proceeds simultaneously with its breakdown (at isolated points), hence causing the rate of attack to fall off, under supersaturated conditions very little strengthening of the hydroxide film takes place after its initial formation; thus, breakdown of the film proceeds at a greater pace than its strengthening—hence the concave type of curve. When all the potentially active centres have been opened up and rusting is proceeding on practically all available points, acceleration of the attack ceases and an essentially linear relationship is assumed. This linearity is probably characteristic of the attack at any one rust centre, but for the reasons given it is shown by the mean weight-increment of the specimen only in the later stages.

The appearance of specimens is broadly similar to those in the un-

saturated atmosphere.

The explanation suggested for this rather surprising result is as follows. In the supersaturated atmosphere a film of moisture is distributed uniformly over the specimen. This encourages the formation of a film of ferrous or ferric hydroxide, replacing the initial air-formed film of oxide, but still invisible. (Such a film has been noted by Bengough, Lee and Wormwell²⁰ for immersed conditions.) At first the hydroxide film presents a greater resistance to the very humid conditions of attack than does the oxide film to the unsaturated

²⁰ W. S. Patterson, *J. Soc. Chem. Ind.*, 1930, 49, 203T.

²⁰ *Proc. Roy. Soc.*, 1931, 134A, 334, 336.

saturated atmosphere of 99 per cent. relative humidity, except that there is a greater degree of spreading from the separate centres. In the later

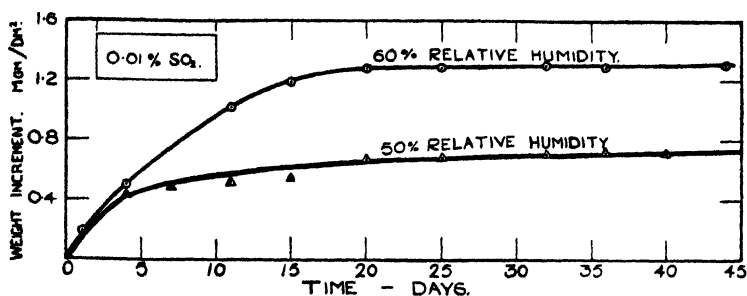


FIG. 8.—Influence of sulphur dioxide at low relative humidity.

stages, moreover, rusting is much more widespread; at 100 days approximately 50 per cent. of the specimen is covered with rust.

INFLUENCE OF SULPHUR DIOXIDE.

Unsaturated Atmospheres.

The experiments were carried out at a uniform concentration of 0.01 per cent. sulphur dioxide.

Constant Relative Humidity.—Time-corrosion curves for 99, 75, and 70 per cent. relative humidities are plotted in Fig. 7. Following an early exponential part, with a very high rate constant, an approximately linear relationship is reached at about twenty-five days (*cf.* purified air results where the attack is linear at first and falls off in the later stages). The “isolated point” type of attack is followed, but the centres are very much closer together than in purified air, and further points develop in the initially intervening spaces. The complete covering of the specimen with rust takes place very rapidly at high humidities—at 99 per cent. R.H. it is completed in the first day, the red rust subsequently developing a purplish hue, especially at the edges. The great increase in the attack brought about by the presence of sulphur dioxide

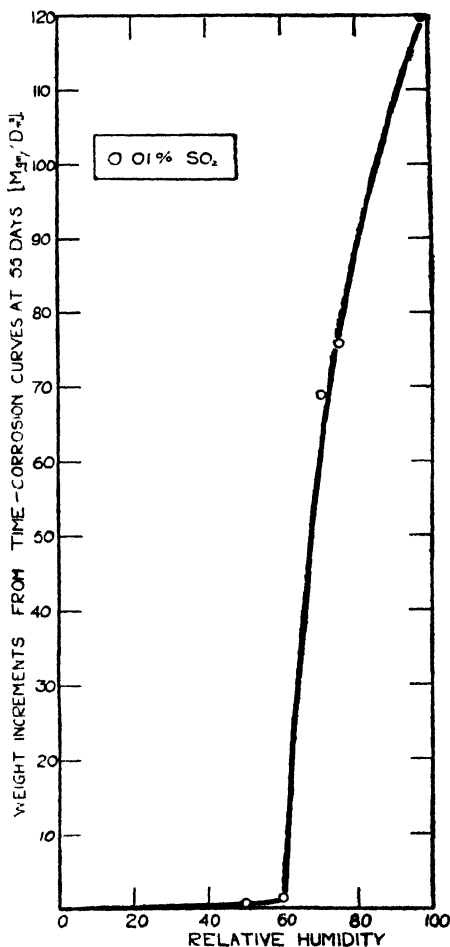


FIG. 9.—Critical humidity as shown by values from time-corrosion curves.

is shown in Fig. 7 by comparison of Curve A with Curve D (replotted from Fig. 6) for purified air of 99 per cent. relative humidity; besides the difference in corrosion values the difference in the form of the curves should be especially observed.

At 60 per cent. and lower relative humidities there is no rusting, and no visible alteration beyond a slight darkening that is discernible only by comparison with freshly cleaned specimens. The weight-increment/time curves for 60 per cent. and 50 per cent. R.H. (Fig. 8) show an almost complete flattening toward the time-axis after about twenty days.

The profound increase in the amount of attack that takes place at the critical humidity (between 60 and 70 per cent. R.H.) is shown in Fig. 9, where the corrosion values at fifty-five days (approximately the latest common time on the curves in Figs. 7 and 8) are plotted against relative humidity. Bearing in mind that the upper points represent values that are themselves increasing with time, it is evident that on this method of

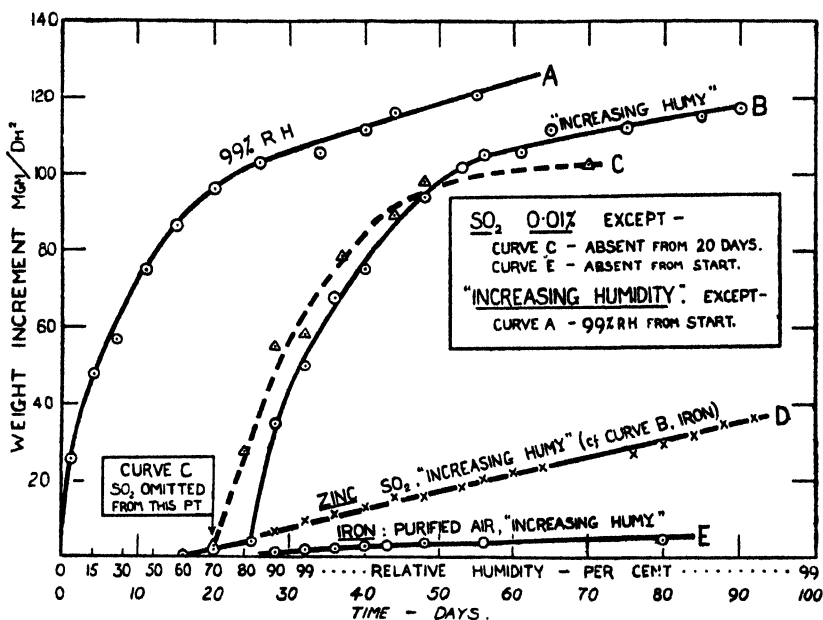


FIG. 10.—Influence of sulphur dioxide at constant and "increasing" relative humidity. Critical humidity shown by "increasing humidity" curves.

assessment the effect will become even more marked for longer periods of the individual experiments.

Increasing Relative Humidity.—Fig. 10 (Curve B) shows the effect of exposing specimens to an atmosphere the relative humidity of which is increased in steps during the progress of the experiment, from zero at start to a maximum (maintained for the rest of the experiment) of 99 per cent. at thirty-six days (cf. Curve B, Fig. 6). Plotting the earlier values (too small to be shown in Fig. 10) on a more open scale, as in Fig. 11, shows this first pronounced increase in the corrosion rate more clearly. It occurs immediately following the increase of the relative humidity from 50 to 60 per cent.; but visible rust does not appear on the specimen until 70 per cent. relative humidity has been reached. There seems little doubt that the marked increase in weight at 60 per cent. R.H. must be bound up with the series of changes that immediately follows, even though it does not coincide with the appearance of rust; possibly it is associated with

the point at which water is first adsorbed on the surface.²¹ The development of rust at a slightly later stage does not give rise to any appreciable break; but an extraordinarily marked break does occur when the humidity reaches 80 per cent.²² (at twenty-four days under the conditions of the experiment—see Curve B, Fig. 10). This phenomenon, the genuineness of which has been verified by a number of repeat experiments, is believed to afford confirmation of the hypothesis advanced by Patterson and Hebbs,²³ based on Zsigmondy's theory of gel structure. Thus, assuming that the rust formed near the lower end of the critical humidity range has a gel structure, the water it contains is not free to participate in the furtherance of corrosion. On hypothesis, both rust and water in the capillaries are in a state of mutual compression, and the radius of curvature of the surface of water in the capillaries has its smallest possible value. At the higher limit of the critical humidity range the capillaries commence to fill with water, the state of compression is released, and water is free to pass from the surface of the rust to the surface of the metal. Thus, an excessively small increment in the actual water content of the rust leads to a very much greater increase in the rate of attack. On this view, whilst the beginning of the critical humidity range (the "primary critical humidity") depends on an optimum relationship between water vapour and sulphur dioxide in the atmosphere, its completion at the "secondary critical humidity" is dictated by properties of the rust itself in relation to water vapour only.

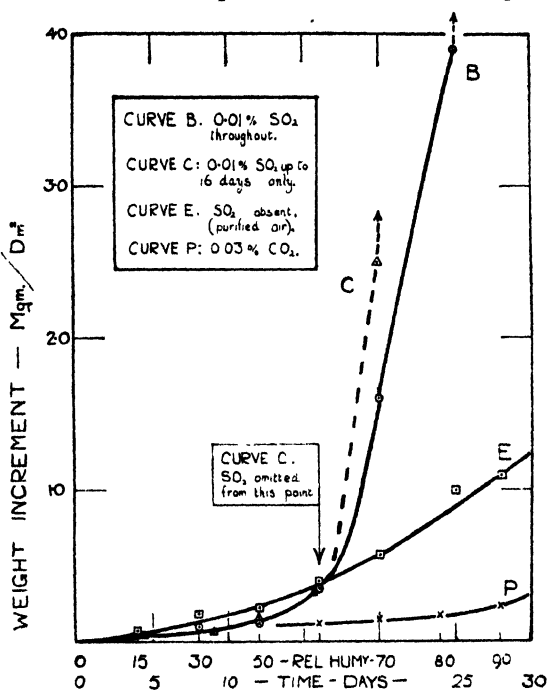


FIG. 11.—Changes in neighbourhood of "primary critical humidity" (iron).

Confirmation of this was obtained by means of an experiment in which sulphur dioxide was withdrawn entirely from the system at the commencement of the critical humidity range (at sixteen days); i.e., from this point onwards an atmosphere of purified air was substituted for the atmosphere

²¹ Further work on this question is desirable, particularly from the point of view of the precise part played by sulphur dioxide. In the case of nickel (Vernon, *J. Inst. Metals*, 1932, 48, 121—also unpublished experiments) it has been shown fairly conclusively that adsorption of sulphur dioxide precedes adsorption of water, before any visible effect is observed.

²² This is not necessarily the precise value of the "secondary" critical humidity, since in the experiments (throughout which the uniform sequence of humidity changes was intentionally preserved) no intermediate value between 70 and 80 per cent. relative humidity was tried.

²³ *Trans. Faraday Soc.*, 1931, 27, 277.

containing 0.01 per cent. SO_2 , the same sequence of humidity changes being continued. The results are shown in Curve C, Fig. 10. Rate of attack immediately after withdrawal of SO_2 , so far from suffering any diminution, is actually increased, whilst the corrosion value at the close of the experiment is similar to, or only very slightly less than, that obtained when sulphur dioxide is present for the whole time. On the other hand, the dependence of the final value on the presence of traces of sulphur dioxide in the early stages, is shown by comparison with Curve E (a re-plot of Curve B, Fig. 6) which represents the effect of precisely similar humidity changes in the complete absence of sulphur dioxide.

The appearance of specimens in the later stages of the "increasing humidity" experiments is similar to those in the experiments employing a humidity of 99 per cent. from the start; in both cases the specimens are covered with red rust which, however, has a slight purplish tint, especially at the edges. To assist comparison, the curve for the 0.01 per cent. sulphur dioxide atmosphere at 99 per cent. constant humidity is replotted at A; thus, Curves A and B, Fig. 10, are comparable with Curves A and B,

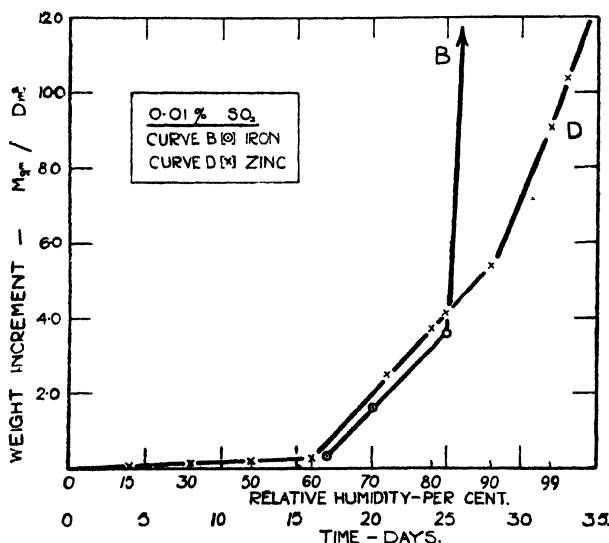


FIG. 12.—Changes at primary and secondary critical humidities (iron and zinc).

result for purified air—no doubt lies in the action of sulphur dioxide; either below the critical humidity, by destroying the protective properties which the primary film would otherwise possess, or, more probably, above the critical humidity, by breaking down rapidly the primary film which, in purified air, would afford substantial protection.

In view of its technical importance as a protective covering metal for iron, a few comparative experiments have been carried out on zinc, e.g., Curve D, Fig. 10; this represents conditions of "increasing humidity," again in presence of 0.01 per cent. sulphur dioxide (zinc sheet containing 99.7 per cent. Zn was used; dimensions and preparation of specimens as for iron). It is evident that for the major part a linear relationship is followed; also that any change arising from the increase in humidity from 0 to 99 per cent. is comparatively small. To avoid confusion, however, the early part of the curve is omitted from Fig. 10 and plotted, together with early part of Curve B (iron), on a more open vertical scale in Fig. 12. The primary and secondary critical humidities both for iron and for zinc,

Fig. 6. In Fig. 10 the latter parts of the curves are approximately equal in magnitude and slope; i.e., so far as the ultimate corrosion value is concerned it is immaterial whether the relative humidity is maintained at 99 per cent. from the start or whether it is increased gradually up to this value. The explanation of this result—particularly the marked contrast it presents with the corresponding

are here brought out clearly. Quantitatively the effect at the primary critical humidity is approximately the same for zinc as for iron; moreover, over the narrow range between the two changes of slope the curves are almost exactly parallel. At the secondary critical humidity, however, the magnitude of the change is of an altogether lower order of magnitude for zinc than for iron. Zinc specimens under the conditions of these experiments undergo a fairly rapid loss of reflectivity, particularly when the critical humidity period is passed; in the later stages a white corrosion product appears.

The relationships of iron, zinc, and copper under the present conditions (0.01 per cent. SO_2 , "increasing humidity" in the early stages) are shown in Fig. 13, where characteristic curves are plotted; the flattening of the copper curve in the later stages confirms results previously reported.⁵⁴

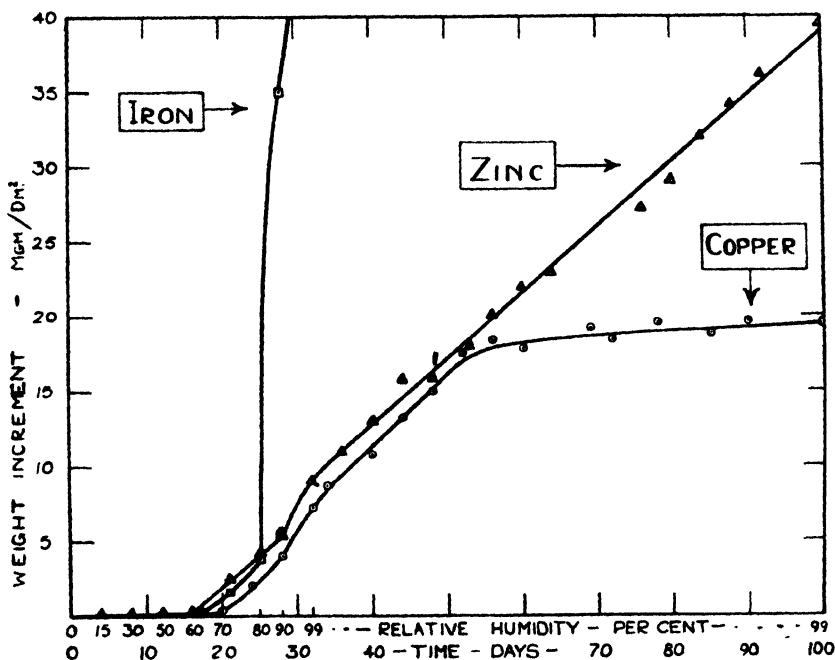


FIG. 13.—Relative behaviour of iron, zinc and copper (0.01 per cent. SO_2 ; increasing humidity in early stages).

"Supersaturated" Atmospheres.

The influence of sulphur dioxide under conditions such that gross films of moisture may be precipitated from atmospheres supersaturated with respect to water vapour was investigated by means of Hempel desiccators (5000 c.c. capacity) as used in the previous work.⁵⁵ The specimens having been introduced, the vessel was evacuated and refilled with air at a relative humidity of 10 per cent. at 25°. Before atmospheric pressure was reached, the appropriate volume of sulphur dioxide (previously mixed with purified air) was admitted, and 50 c.c. of distilled (conductivity) water was introduced through the stopcock into the annular reservoir. The preliminary humidification of the air was not carried to saturation for the reason that the humidifying temperature (25°) was higher than room temperature

⁵⁴ Part I. of present series. *Trans. Faraday Soc.*, 1931, **27**, 260.

⁵⁵ *Ibid.*, p. 267.

(approximately 20°) ; but as the water added was also at 25° saturation would be very quickly reached within the vessel itself on exposure to room conditions. The vessels were shielded from direct sunlight but not thermostated.

In one group of experiments sufficient sulphur dioxide (5 c.c.) was introduced to give a nominal (initial) concentration of 0.1 per cent. Taking into account the amount of gas dissolving in the water (but excluding that taken up in the corrosion process) the mean concentration of sulphur dioxide in the atmosphere was approximately 0.07 per cent. Similarly, in other experiments in which 0.5 c.c. of sulphur dioxide was introduced (nominally 0.01 per cent.), the mean concentration was approximately 0.007 per cent. Both atmosphere and liquid were replenished on each occasion the specimens were removed for weighing.

Results for the two concentrations, compared with those for purified air (Fig. 22), show the extraordinarily stimulative influence of traces of sulphur dioxide under supersaturated conditions. At six days the specimens in the atmosphere containing " < 0.1 per cent. SO_2 " were completely covered with rust ; at twenty-seven days the apparent thickness of the specimens, owing to the accumulation of rust, was approximately three times the original thickness. Yet not only did the rust adhere, but the attack on the metal continued at an undiminished rate. Up to 160 days (experiment still continuing) the linearity of the time/corrosion curve is remarkable, having regard to the uncontrolled conditions and the great accumulation of rust—giving a weight-increment of no less than 3.6 grams per sq. decim. (1.8 grams per specimen). Similar observations apply to the results for the atmosphere containing " < 0.01 per cent. SO_2 " except for the longer times taken—*i.e.*, twenty days to become completely covered, and an apparent thickness of twice the original at forty-two days ; when once the specimen is covered with rust, a surprisingly constant rate is followed (Fig. 22), although in this case there is a slight change of slope at seventy-six days.

INFLUENCE OF PRECIPITATED SOLID PARTICLES.

It was shown in the earlier work⁽⁶⁾ that suspended particles in the air play a very important part in atmospheric rusting, which may even, in some circumstances, be entirely suppressed by their exclusion. Subsequent work⁸ has suggested that in urban atmospheres ammonium sulphate is largely responsible ; further information, however, concerning the nature of such suspended particles is much to be desired. A welcome contribution has been made by Drexler,²⁶ who considers that the structure of the rust is determined by the nature of the rust-forming nuclei. This author recognises two varieties of ferric hydroxide, α and γ $\text{FeO}(\text{OH})$, which, with magnetite, are constituents of atmospheric rust. The α form is believed to be set up by non-dissociated substances such as gypsum and ash particles, and the γ form by highly dissociated substances such as ammonium sulphate and ammonium chloride.

It is evident that suspended particles which come into consideration must fall into three main groups according as they are (1) intrinsically active, *e.g.*, dissociating mineral salts ; (2) intrinsically neutral, but capable of absorbing active gases from the atmosphere, *e.g.*, various forms of amorphous carbon ; (3) intrinsically neutral, with negligible capacity of absorption, *e.g.*, crystalline silica.

As the experiments now reported do not claim to be exhaustive, but aim rather at a preliminary survey of the field, one typical representative only of each group has been examined, *i.e.*, ammonium sulphate, sugar charcoal,²⁷ powdered quartz.

²⁶ F. Drexler, *Korr. u. Metallschutz*, 1930, 6, 3.

²⁷ The author is much indebted to Mr. Alexander King, M.Sc., Imperial College of Science, for the supply of a specially prepared sugar charcoal, having very reproducible properties, for use in these experiments.

The method adopted for "inoculating" the surface of the specimen with the particles under examination has consisted in dipping the cleaned and weighed specimen into pure carbon tetrachloride containing a suspension of the powdered material, previously sieved through a double thickness of muslin; the mixture was heated to approximately 40° C. to facilitate stirring of particles and evaporation of reagent on removal. The amount of material in suspension was regulated so that, on removing the specimen, an approximately constant weight of 0.2 mg. (0.4 mg./dm.²) was uniformly distributed over the whole surface. (See typical figures, Table V.) The error in the amount on individual specimens rarely exceeded 0.02 mg., and in no case was there reason for believing that any departure from the standard "inoculation" had affected appreciably the ultimate result.²²

TABLE III.—TYPICAL RESULTS FROM "INCREASING HUMIDITY" EXPERIMENTS.

(Weight-increments in Mgms. Area of specimen, 0.5 Sq. Dm.)

Days Exposed.	Humidity at Previous Replacement.	Purified Air. Fig. 6, Curve B; Fig. 19, Curve B.		0.03 per cent. CO ₂ . Fig. 19, Curve D.		0.01 per cent. SO ₂ . Fig. 10, Curve B.	
		Expt. 32.	Expt. 50.	Expt. 44.	Expt. 49.	Expt. 24.	Expts. 48/91.
4	0	0.039 } 0.027 } 0.033	0.032 } 0.035 } 0.033	0.018 } 0.027 } 0.022	0.011 } 0.027 } 0.02	0.010 } 0.010 } 0.010	0.013 } 0.018 } 0.015
8	15	0.127 } 0.111 } 0.119	0.099 } 0.088 } 0.094	0.029 } 0.040 } 0.035	0.035 } 0.033 } 0.034	0.045 } 0.021 } 0.033	0.030 } 0.046 } 0.056
12	30	0.109 } 0.112 } 0.110	0.102 } 0.128 } 0.115	0.049 } 0.060 } 0.055	0.097 } 0.037 } 0.06	0.050 } 0.068 } 0.059	0.062 } 0.050 } 0.056
16	50	0.197 } 0.150 } 0.173	0.202 } 0.207 } 0.204	0.042 } 0.075 } 0.06	0.074 } 0.044 } 0.06	0.123 } 0.201 } 0.162	0.180 } 0.144 } 0.162
20	60	0.332 } 0.295 } 0.31	0.264 } 0.319 } 0.29	0.085 } 0.070 } 0.08	0.099 } 0.052 } 0.075	0.799 } 0.755 } 0.777	0.756 } 0.800 } 0.778
24	70	0.514 } 0.489 } 0.50	0.507 } 0.495 } 0.50	0.074 } 0.093 } 0.085	0.080 } 0.113 } 0.095	1.95 } 1.95 } 1.95	1.91 } 1.87 } 1.89
28	80	0.688 } 0.425 } 0.555	0.510 } 0.578 } 0.544	0.115 } 0.109 } 0.112	0.135 } 0.118 } 0.125	15.72 } 18.15 } 16.93	19.23 } 16.39 } 17.80
32	90	0.744 } 0.645 } 0.71	0.76 } 0.65 } 0.70	0.250 } 0.239 } 0.245	0.231 } 0.223 } 0.225	23.77 } 24.60 } 24.19	25.50 } 24.20 } 24.85
36	99	1.065 } 0.625 } 0.845	0.851 } 0.856 } 0.853	0.318 } 0.456 } 0.39	0.375 } 0.459 } 0.41	32.70 } 33.70 } 33.20	34.71 } 32.95 } 33.83
40	99	1.34 } 1.24 } 1.29	1.14 } 1.13 } 1.135	0.458 } 0.544 } 0.50	0.518 } 0.486 } 0.50	36.06 } 38.55 } 37.30	38.44 } 37.00 } 37.72
48	99	1.72 } 1.82 } 1.77	1.77 } 1.77 } 1.77	0.510 } 0.553 } 0.53	0.580 } 0.519 } 0.55	49.73 } 45.49 } 47.61	47.31 } 46.59 } 46.95
56	99	1.79 } 1.84 } 1.81	1.85 } 1.82 } 1.83 } 1.73 } 1.81	0.513 } 0.539 } 0.53	0.636 } 0.538 } 0.59	53.25 } 53.66 } 51.92 } 52.96 } 52.95	51.83 } 51.79 } 51.81

²² It is hoped later to reproduce an important condition of service, in which the present method falls short, i.e., the precipitation of particles on to the surface during the whole period of exposure.

TABLE IV.—TYPICAL RESULTS FROM "SUPERSATURATED" EXPERIMENTS.

Distilled Water within Vessel; Atmosphere and Specimens as Stated. Weight-increments in Mgms. Area of Specimen, 0.5 Sq. Dm.

(For Weight of $(\text{NH}_4)_2\text{SO}_4$ on "Inoculated" Specimens, see Table V.)

Days Exposed.	Purified Air. $(\text{NH}_4)_2\text{SO}_4$ present (Figs. 22 and 23).	0.1 per cent. CO_2 $(\text{NH}_4)_2\text{SO}_4$ present (Fig. 22).	0.1 per cent. SO_2 $(\text{NH}_4)_2\text{SO}_4$ present (Fig. 23).	0.1 per cent. SO_2 $(\text{NH}_4)_2\text{SO}_4$ absent (Fig. 22).	0.01 per cent. SO_2 $(\text{NH}_4)_2\text{SO}_4$ present (Fig. 22).	0.01 per cent. SO_2 $(\text{NH}_4)_2\text{SO}_4$ absent (Fig. 22).
	Expt. 136.	Expt. 139.	Expt. 138.	Expt. 141.	Expt. 137.	Expt. 140.
6	15.26 15.83 12.54 11.89 } 13.88	5.17 5.44 6.05 4.29 } 5.23	96.36 96.90 116.73 93.87 } 101.0	208.1 198.1 183.0 186.9 } 194.0*	24.92 27.76 26.89 26.94 } 26.6	42.80 34.59 36.11 32.21 } 36.4*
14	20.95 20.53 17.27 17.68 } 19.15	8.81 9.13 9.52 7.02 } 8.62	226.0 213.5 239.2 259.8 } 234.6	254.3 226.0 229.1 234.7 } 236.0	53.53 52.76 57.37 57.47 } 55.3	76.00 78.89 64.37 64.12 } 71.0
20	24.41 24.32 20.45 21.18 } 22.6	10.33 10.76 11.76 8.56 } 10.35	268.7 278.8 289.3 301.0 } 284.5	281.6 265.7 263.6 239.8 } 262.7	77.04 78.68 67.05 70.22 } 73.3	83.96 85.64 71.53 71.10 } 78.1
27	28.02 26.88 24.65 24.63 } 26.05	11.60 11.92 13.07 9.63 } 11.55	325.6 346.6 365.3 370.4 } 352.0	295.7 320.6 331.9 250.0 } 297.0	90.8 92.4 81.4 92.2 } 89.2	98.6 100.7 87.0 87.5 } 93.5
42	31.25 30.26 27.44 29.01 } 29.5	12.98 13.38 14.47 10.04 } 12.72	449.4 474.6 494.0 498.0 } 479.0	416.9 487.1 487.0 382.1 } 443.2	120.9 118.6 107.4 132.5 } 119.9	142.6 141.2 126.0 129.0 } 134.7
55	36.64 34.88 31.04 33.51 } 34.0	14.07 14.54 15.82 12.01 } 14.11	570.1 607.9 625.8 615.2 } 605.0	679.9 645.4 646.4 552.6 } 631.0	165.4 160.3 142.8 161.9 } 157.6	172.6 173.7 158.8 181.1 } 171.5
76	45.15 45.54 37.16 41.19 } 42.3	16.82 16.91 17.52 14.01 } 16.3	761.5 810.8 895.0 855.6 } 881.0	943.8 932.3 918.3 829.4 } 906.0	210.1 212.5 192.8 207.8 } 206.0	224.9 230.9 214.1 209.2 } 220.0

* Seven days.

TABLE V.—WEIGHT OF $(\text{NH}_4)_2\text{SO}_4$ (MGMS.) ON "INOCULATED" SPECIMENS (TABLE IV.).

Expt. 136.	Expt. 139.	Expt. 138.	Expt. 137.
0.195	0.200	0.198	0.201
0.207	0.184	0.187	0.206
0.195	0.201	0.191	0.191
0.213	0.212	0.207	0.183

(a) Experiments in Purified Air.

Unsaturated Atmospheres.

Ammonium Sulphate Particles.—Results obtained at constant relative humidities of 99 per cent. and 90 per cent. respectively on specimens initially impregnated with ammonium sulphate particles are plotted at A and C, Fig. 14. Similar types of

results were obtained at other values above the critical humidity, the

curves in each case "flattening out" completely in the later stages. Fairly large rust spots developed at each of the "inoculated" centres after the first day, and within the first few days the specimens had assumed an appearance characteristic of the present conditions—i.e., curious hair-like lines of rust radiated from each centre and joined up with other "hair-marks" from other centres. (See Fig. 15, B. A somewhat similar appearance is presented by specimens under ordinary room conditions.)³⁹ At about seven days approximately half the total area at 99 per cent. relative humidity (rather less at 90 per cent.) was covered with rust, the intervening spaces remaining bright; but neither the distribution nor the intensity of rusting was appreciably different at seventy days. Evidently, therefore, the rust which forms when the relative humidity is maintained from the outset consistently above the critical humidity does not of itself facilitate further rusting.

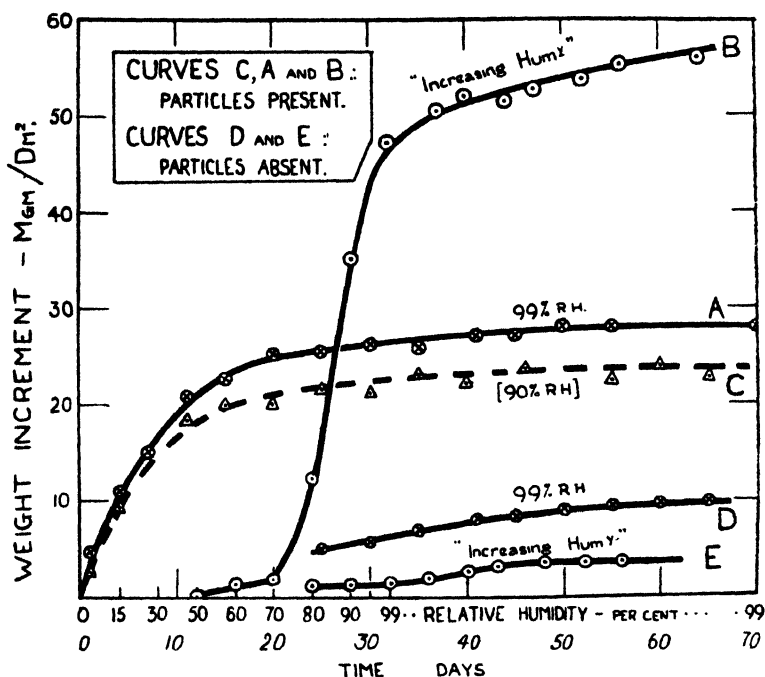


FIG. 14.—Influence of ammonium sulphate on the rusting of iron in purified air (constant and "increasing" rel. humidity).

A very different state of affairs is shown by Curve B, which represents the effect of "increasing humidity" (humidity increased in steps over the first part as in previous examples). This has yielded a corrosion value *approximately double* that given by the "constant humidity" conditions (a ratio that is actually increasing with time). This result is in striking contrast with comparable results in the absence of particles; e.g., in presence of sulphur dioxide, where the two curves give approximately identical values (Fig. 10, A and B), and more especially in purified air (Fig. 6, A and B) where increasing humidity gives *approximately only half* (in decreasing ratio) the corrosion value of the constant humidity conditions.

The interpretation is doubtless to be associated with changes occurring in the critical humidity range. It is clear from the early part of Curve B

³⁹ See Fig. 21 of "First Report," *Trans. Faraday Soc.*, 1924, 19, facing p. 887.

(Fig. 14) that the introduction of the salt-particle factor, in just the same way as the introduction of the sulphur-dioxide factor, has brought about well-defined primary and secondary critical humidities, a phenomenon that is absent in the absence of both these factors. The disposition of Curve B over the range in question is, in fact, extraordinarily similar to that of the corresponding curve for the sulphur dioxide atmosphere (Curve B, Fig. 10). In point of time the curve for "particles without sulphur dioxide" precedes that for "sulphur dioxide without particles." This is shown in Fig. 16, where the early stages of the two curves (in neighbourhood of primary critical humidity) are plotted on a much more open scale.

Nevertheless, the similar shape of these curves cannot wholly explain the effect of salt particles on the *final corrosion value*; for (comparing the "increasing humidity" with the "constant humidity" curve) the introduction of sulphur dioxide achieved only approximately equality, not a

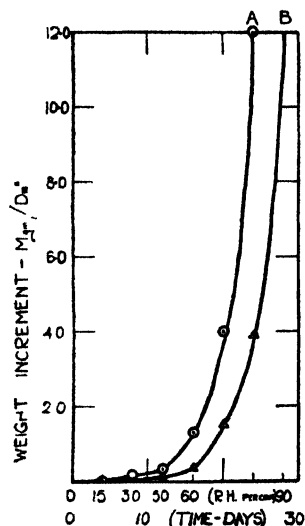


FIG. 16.—Primary critical humidity.

- A. $(\text{NH}_4)_2\text{SO}_4$ particles; purified air.
- B. "Blank" specimen; 0.01 per cent. SO_2 .

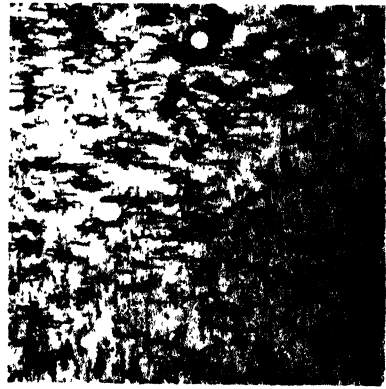
complete reversal. In other words, it cannot be solely a matter of breaking down the protective film formed below the critical humidity. This factor is believed to be supplemented by factors connected with the properties of the rust in the two cases. Thus, in the presence of salt particles (but probably not at all in their absence) the structure of the ferric hydroxide gel may differ very greatly according to whether relatively large quantities of moisture are supplied at the outset, with consequent tendency to dissolve the particles, or whether they are allowed to remain intact throughout the critical humidity period. In the latter case, the particles will act both chemically and physically; chemically in promoting the attack on the metal and forming the primary rust, physically in helping to give the primary rust a more open and attenuated structure (*e.g.*, surface tension effects, causing the rust to adhere to the particle rather than to the metal) hence providing a more efficient medium and intensifying the effect of the secondary critical humidity. Quantitatively, the influence of salt particles at 99 per cent. R.H. is shown in Fig. 14 by the comparison of the latter parts of curves A and D (constant humidity from the start), and curves B and E (increasing humidity in the early stages).

Ammonium Sulphate Particles on Zinc.—Results for zinc in purified air ("increasing humidity"), with and without the presence of ammonium sulphate particles, are shown in Curves A and B, Fig. 17. Over the first part the two curves are coincident; even in the later stages the one curve (particles present) lies only very slightly above the other. The corrosion values are very small (*cf.* vertical scales); and whilst the experiments are not exhaustive, it is evident that any effect due to the presence of ammonium sulphate particles is extremely slight. This again reveals a fundamental difference between the behaviour of iron and zinc.

Silica and Charcoal Particles on Iron.—Experiments with powdered silica and with powdered charcoal, in atmospheres maintained continuously at 99 per cent. R.H. and also in atmospheres of increasing humidity, have shown no effect either visually or quantitatively (so long as purified air was used) that could be attributed to the presence of the



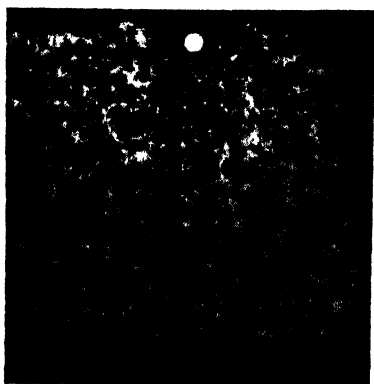
A "Blank"



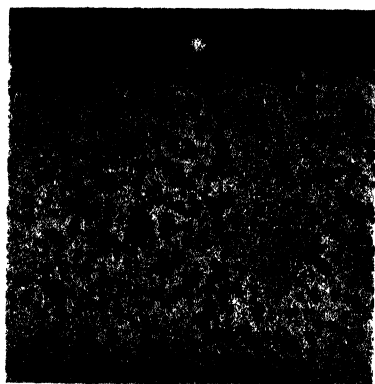
B "Inoculated"

FIG. 15 - Influence of ammonium sulphate particles in purified air (99 per cent RH), 70 days' exposure, 0.1 mg "particles" on face of specimen (initially). Photographs actual size.

(To face page 1690.



A. Purified air.



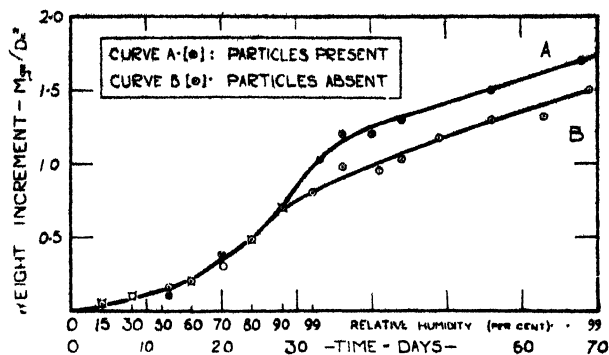
B. Air containing CO_2 .

FIG. 21 Influence of carbon dioxide supersaturated conditions, 64 days' exposure. Concentration of CO_2 in experiment (B) was rather less than 3 per cent., but concentrations of less than 0.1 per cent. gave very similar results.

[See page 1695]

particles; time-corrosion curves were indistinguishable from those yielded by blank specimens. Thus, although a partial physical mechanism has been attributed to the action of ammonium sulphate particles, this would appear to depend on their being themselves able to initiate corrosion; i.e., the particles must be capable of affecting the primary critical humidity if they are to have any appreciable subsequent influence. Much, however, depends on the purity of the air (e.g., results under "b" *infra*)

FIG. 17.—Influence of ammonium sulphate particles on corrosion of zinc in purified air. (Increasing humidity in early stages)



"Supersaturated" Atmospheres.

The characteristic "concavity" of the early part of the time-corrosion curve, under supersaturated conditions in the absence of particles, has already been discussed. The effect of initially inoculating the specimen with ammonium sulphate particles is also characteristic, in that it converts the initial concavity (about the vertical axis) into a marked convexity. Actually, just as the "concavity" may take the form of several concave branches, so the "convexity" usually consists of a series of "humps," the breaks in the curves probably depending in each case on fluctuations in temperature. Typical results, with and without particles, are shown in Curves A and B, Fig 20

(b) Air containing Sulphur Dioxide.

Unsaturated Atmospheres.

Ammonium Sulphate, Charcoal and Silica Particles.—Results of experiments with particles of each of the substances under investigation in an atmosphere containing 0.01 per cent. sulphur dioxide are plotted in Fig. 18. The "increasing humidity" curves (D, E, G) present several interesting features. First, up to the point at which the secondary critical humidity occurs they are coincident, not only with each other, but also with Curve C for blank specimens free from particles. This is true even for ammonium sulphate, the characteristic curve for which (in the absence of sulphur dioxide) lies to the left of that shown in the figure. Evidently sulphur dioxide, at the concentration employed, is able to impress its own characteristics on each of the curves so far as the primary critical humidity is concerned. At the secondary critical humidity, however, extraordinarily marked differentiation occurs.

Taking Curve C (particles absent) as the standard of reference, then the presence of silica particles (Curve D) has only a slight effect. The increase as compared with the (negligible) effect of such particles in purified air is probably associated with the much greater amount of rust on the specimen, combined with the tendency of the inert particles to keep the product more open and hence to facilitate access to the atmosphere; clearly, however, it is not an important factor. On the other hand, ammonium

sulphate particles (Curve E) have a very marked effect, as would be expected from their influence *per se* in purified air, the curve for which is reproduced in the same diagram (Curve B); examination of the two curves shows, in fact, that the two effects are almost exactly additive.

At 100 days the "increasing humidity curve" for ammonium sulphate has reached very nearly the same value as that of the "constant humidity curve" (99 per cent. R.H., Curve F); but as the latter part of Curve E has an appreciable slope, whilst Curve F is then almost flat, it is evident

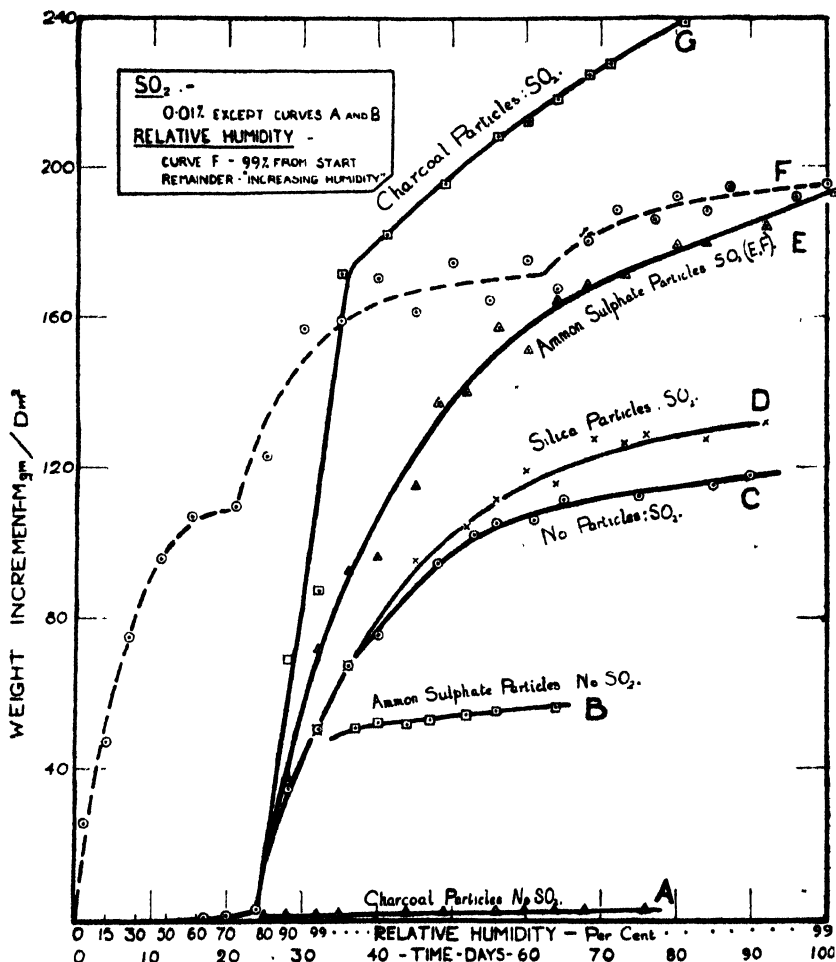


FIG. 18.—Influence of particles on rusting of iron in presence of sulphur dioxide.

that more prolonged exposure would bring Curve E above Curve F (*cf.* Curves C and A, Fig. 14). The partially physical interpretation advanced for the similar effect in purified air probably still holds; that the effect is not so marked may be due to chemical reaction between ammonium sulphate and sulphur dioxide, which would be expected to modify any physical effect due to the original particles.

The outstanding feature of Fig. 18 is doubtless the extraordinary influence of sugar charcoal (Curve G). This not only greatly transcends

the influence of ammonium sulphate under the present conditions, but it is the more remarkable in that sugar charcoal, unlike ammonium sulphate, has no "intrinsic" effect; the behaviour in purified air of specimens impregnated with charcoal (actually identical with that of blank specimens) is shown at A. The comparison of Curves G and A emphasises the enormously important part that may be played by traces of sulphur dioxide in the atmosphere *in the presence of particles that are capable of absorbing this gas*. The visual results are equally striking. At forty days, whilst inoculated specimens in purified air are still apparently bright, those in the atmosphere containing 0.01 per cent. sulphur dioxide are completely covered with rust. Owing to this rapid lateral spreading, the period during which the characteristic isolated rust points may be observed is greatly reduced in the presence of the charcoal particles. This corresponds with the very steep portion of the time-corrosion curve immediately following the secondary critical humidity; when once the specimen is covered with rust there is an abrupt change in the slope of the curve and a lower and approximately constant value is assumed.

"Supersaturated" Atmospheres.

The profound influence of traces of sulphur dioxide under supersaturated conditions (p. 1685), appears to be modified to a negligible extent by the presence of solid particles. This is shown for ammonium sulphate in Fig. 22. Experiments at each concentration of sulphur dioxide (nominally 0.1 and 0.01 per cent.) included specimens both in the initially-clean condition and "inoculated" with 0.2 mg. ammonium sulphate. Results for each group of specimens fall, within experimental error, on the same curves. Evidently it is under conditions such that the rate of attack is *in any case* very great that the influence of particles is felt to the least extent.

(c) Air containing Carbon Dioxide.

The influence of solid particles in presence of carbon dioxide is discussed later (see p. 1694).

INFLUENCE OF CARBON DIOXIDE.

The experiments hitherto discussed have employed air from which carbon dioxide has been completely removed in the purification train. Experiments in which definite concentrations of carbon dioxide have been added to the atmosphere under test have yielded results that directly conflict with long-accepted views on the influence of this constituent.

Unsaturated Atmospheres.

Results for atmospheres of 99 per cent. constant humidity and "increasing humidity" up to 99 per cent., in the absence and in the presence of 0.03 per cent. carbon dioxide (the normal atmospheric content), are plotted in Fig. 19. The carbon dioxide was prepared by the action of phosphoric acid on sodium carbonate, both reagents of high purity, so that contamination with any other acid vapour was avoided. The curves show a relatively enormous *depression of corrosion* due to the presence of carbon dioxide, amounting, at eighty days, to 80 per cent. (10.4 to 2.08) and 75 per cent. (4.64 to 1.16) for the constant and increasing relative humidities respectively. Moreover, since the curves are steeper in the case of the atmospheres free from carbon dioxide the effect may be expected to become even more pronounced with increasing time.

The amount of rust on specimens in the presence of carbon dioxide is exceedingly small, and is usually confined to the neighbourhood of the edges. In the case of the increasing humidity conditions, the whole of

the rusting takes place at the rather ill-defined critical humidity in the neighbourhood of 80 per cent. R.H.; from this point onwards rusting is suppressed, and there is no further change in the appearance of the specimen. Even below the critical humidity, however, weight-increments are smaller in the presence of carbon dioxide (see also Fig. 11, Curves E and P, where the early part of Curves B and D are plotted on a more open scale).

"Supersaturated" Atmospheres.

The influence of carbon dioxide under "supersaturated" conditions was investigated by the same method as for sulphur dioxide (p. 1685). Two groups of experiments were carried out at initial concentrations of 3 per cent. and 0.1 per cent. respectively. (Actual mean concentrations were slightly less than these values on account of absorption of carbon dioxide by the water in the vessel.) The higher concentration was intended to be roughly comparable, from the point of view of the large excess of CO_2 over

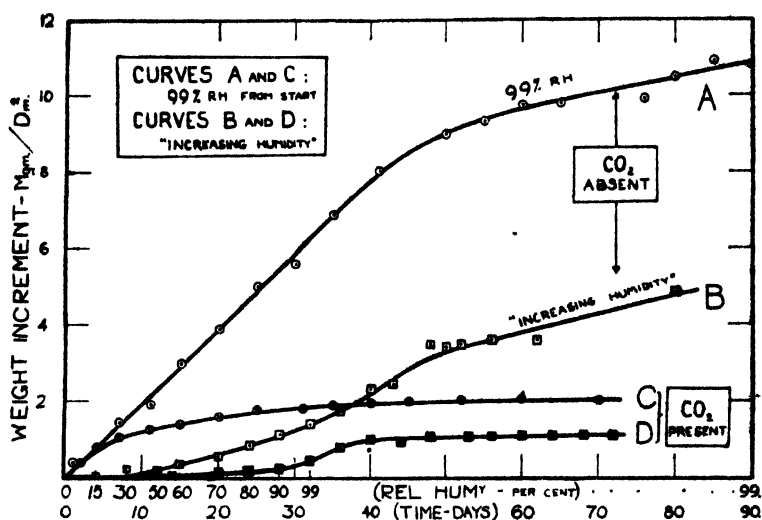


FIG. 19.—Influence of carbon dioxide (0.03 per cent.) on rusting of iron (constant and "increasing" relative humidity).

SO_2 that normally obtains in the atmosphere, with the concentrations of sulphur dioxide employed in the experiments, whilst the lower concentration was directly comparable with the similar nominal concentration of sulphur dioxide in the experiments, and also with the higher limits of carbon dioxide actually occurring in the atmosphere. Each group of experiments included both initially clean specimens and specimens initially impregnated with 0.2 mg. ammonium sulphate.

Impregnated specimens developed rust-spots very quickly (within two hours), clean specimens more slowly (rusting at edges only at seven days); but in all cases rusting was markedly less in the presence of carbon dioxide. This repressive effect was accentuated at longer periods of exposure, and was more pronounced in the case of the "inoculated" specimens. This is shown for the higher concentrations of carbon dioxide in Fig. 20, for which the results in the absence of CO_2 (Curves A and B) have already been discussed. The influence of carbon dioxide appears to be directed largely towards the suppression of the characteristic "humps" introduced into the time-corrosion curve by the presence of particles; hence, although the curves for clean and "inoculated" specimens are still concave and convex about the vertical axis the difference is not so marked in the presence of

carbon dioxide. Photographs of typical specimens after sixty-four days' exposure are reproduced in Fig. 21.

Results for the lower concentration of carbon dioxide in the presence of ammonium sulphate particles, for a longer period of exposure are shown in Fig. 23. This figure, which at 160 days shows corrosion depressed to approximately one-third the value in purified air, owing to the presence of < 0.1 per cent. carbon dioxide, should be compared with Fig. 22, which gives the results from similar experiments (carried out side by side), in the presence of sulphur dioxide. Here, at 160 days, corrosion is increased

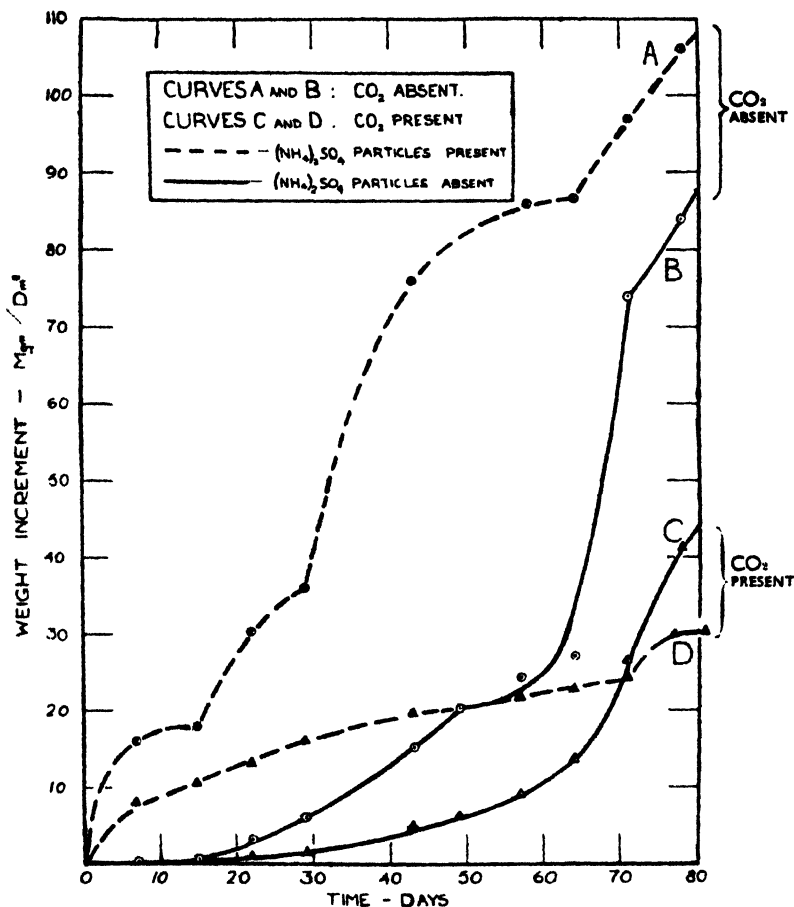


FIG. 20.—Influence of carbon dioxide on rusting of iron (supersaturated conditions) (< 3 per cent. CO_2 , short period).

by approximately five and twenty-eight times the value in purified air by the presence of < 0.01 and < 0.1 per cent. sulphur dioxide respectively. It is noteworthy that whereas the presence of particles does not appreciably modify the stimulative effect of sulphur dioxide, it enhances the restraining influence of carbon dioxide under similar conditions of supersaturation.

Historical and General.

Interest attaches to the restraining influence of carbon dioxide, inasmuch as this substance, even in quite small amounts, has long been

considered to be an active stimulator of the rusting of iron. This was the essential feature of the "acid theory of corrosion," for many years fashionable, and still quite commonly applied to the atmospheric corro-

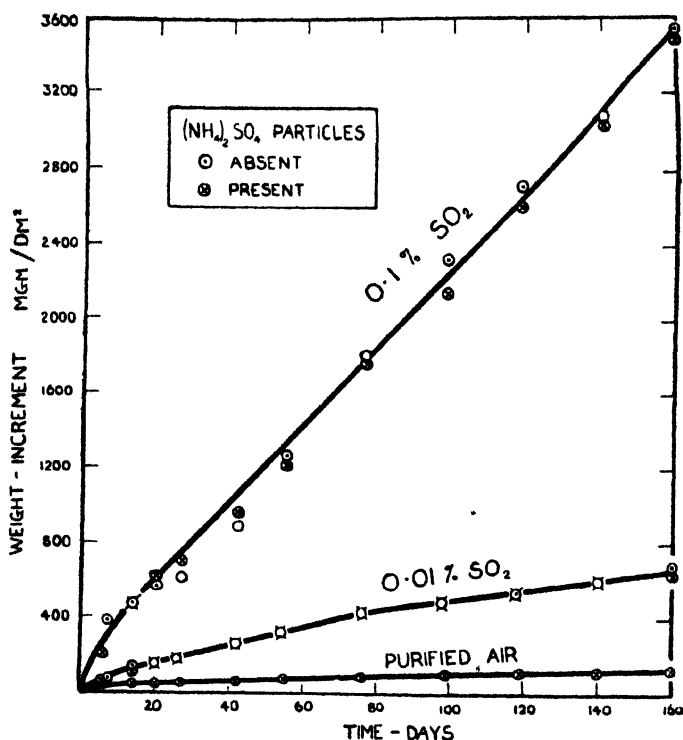


FIG. 22 —Influence of sulphur dioxide on rusting of iron Supersaturated conditions Long period

sion of iron. According to this view, primary attack is due to the joint presence of carbon dioxide, water and oxygen. A trace of carbon dioxide is supposed to permit unlimited attack on iron, for the reason

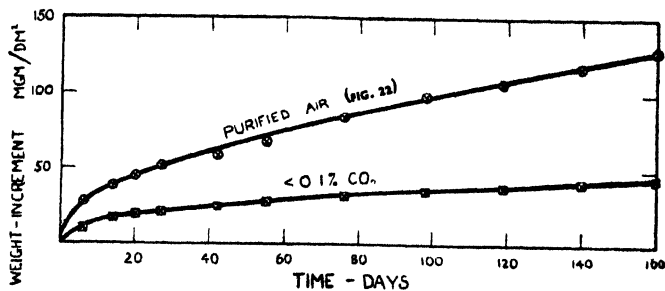


FIG. 23 —Influence of carbon dioxide on rusting of iron (in presence of particles of ammonium sulphate). Supersaturated conditions, < 0.1 per cent. CO₂.

that soluble ferrous carbonate or bicarbonate, on hypothesis the primary product, hydrolyses to give ferric hydroxide, with liberation of carbon dioxide whereby a further equivalent quantity of iron is attacked.

The first postulation of this mechanism is usually attributed to Crum Brown (1888) following experiments by Crace Calvert (1871). The rather meagre published description of Calvert's experiments cannot, however, be held to justify a general theory. Subsequently (particularly between the years 1905 and 1908) elaborate experiments were carried out by other workers to decide the validity of the "carbonic acid theory" and much controversy ensued. Much of this work suffered from over-elaboration. For the crucial point was considered to be whether or not iron would rust at all in the complete absence of carbon dioxide—a purely academic question. The simpler and more vital question, the comparative behaviour of air with and without its normal content of carbon dioxide appears to have been completely overlooked; the possible influence of traces of sulphur dioxide, which may be regarded as a normal constituent of ordinary air, was similarly neglected.

Experiments which were believed to support the view that carbon dioxide is a stimulator of atmospheric rusting have been published by Hicks.⁴⁰ In contrast, however, with much of the earlier work, which centred round the removal of the last traces of carbon dioxide, Hicks went to the other extreme and added concentrations which apparently were very greatly in excess of those present in ordinary air. Although precise details are lacking, there seems little doubt that not only Hicks', but also Calvert's original experiments were vitiated in this way.

Some misconception has probably arisen from the behaviour of iron in concentrated aqueous solutions of carbon dioxide. Tentative experiments in the course of the present work have shown that whereas in a saturated solution of carbon dioxide iron rusts much more rapidly than in distilled water, in dilute solutions the position is reversed; solutions having concentrations respectively one-fifth, one-tenth and one-fiftieth of the saturation value gave corrosion values *less than in distilled water*. (Only in the saturated solution of carbon dioxide was evolution of hydrogen apparent.) Moreover, results lately obtained by Bengough and Wormwell,⁴¹ in their standard apparatus, have shown that the corrosion of iron in *N*/10,000 solutions of NaCl and KCl is less when the overlying air has not been purified than when carbon dioxide (together, of course, with any other acidic gas) has been removed in a purification train.

Under purely atmospheric conditions the present results appear to admit of no doubt that carbon dioxide *per se*, in concentrations not only approximately equal to, but also considerably greater than, the normal atmospheric content, very materially depresses the corrosion rate of iron. Most probably the explanation lies mainly in the modification or destruction of the gel properties of the primary rust; the precise mechanism, however, is a matter for further investigation. Possibly the change in properties is associated with the formation of a basic carbonate more stable under the particular conditions than is commonly supposed. The action of ammonium sulphate particles in intensifying the effect may then be due simply to their facilitating the supply of hydroxide for conversion into basic carbonate, which, on this view, must always be a secondary and not a primary product. Thus, if carbon dioxide is present in sufficient concentration (far higher than is likely in practice) to attack the iron, the attack proceeds at a greater pace than in its absence; but under conditions such that carbon dioxide merely modifies the hydroxide

⁴⁰ J. F. G. Hicks, *J. Physical Chem.*, 1929, **33**, 780.

⁴¹ Third Report of the Corrosion Committee, Iron and Steel Inst., 1935, 150.

that would be formed in any case (the usual state of affairs) its repressive effect is manifested.

SUMMARY.

Part II.

Marked differences in the properties of the oxide film on iron are observed according to whether the film is produced above or below a critical temperature of very nearly 200° . The relation between rate of oxidation and temperature is in accordance with the equation $d \log W/dT = -Q/RT$; but there is a change of constants at 200° giving intersecting straight lines (with increase of slope above the critical temperature) when logs of oxidation rate are plotted against reciprocals of absolute temperature.

At the higher temperatures a parabolic relation between oxidation and time is closely followed ($W^2 = Kt$). The colours produced are consistent with interference of light in a continuous transparent sheath; and any given colour may be obtained at alternative temperatures by calculation of the time required to give the appropriate thickness.

At temperatures below the transition point there is a marked deviation from the quadratic parabola ($W^{2.6} = Kt$, very nearly). The relationship between film thickness and colour no longer obtains; and thicknesses (as deduced from weight-increments) that give interference colours above 200° may be greatly exceeded without appreciable change in appearance. The ill-defined colours that ultimately appear at the higher limits are such as to suggest diffraction in a granular type of film.

At 25° , a point of inflection in the oxidation/time curve at fifteen days, below which deviation from the quadratic parabola is in the reverse direction (index < 2), is believed to mark the completion of the unit lattice of oxide over the whole surface. From this point the parabola is followed closely for a short time. A further point of inflection at which the approximate parabola ($W^{2.6} = Kt$) is assumed, is attributed to the breakdown of a primary film, pseudomorphic with iron, to a secondary film having a granular structure. A similar sequence of changes probably occurs at the higher temperatures (below 200°), but they are completed too rapidly to be followed gravimetrically.

A preliminary examination of certain of the films by electron camera technique (carried out by Mr. G. D. Preston and Dr. L. L. Bircumshaw) has confirmed a change in structure in the neighbourhood of the critical temperature (200°).

Part III.

In purified air of high relative humidity the rusting of mild steel (at isolated centres) is greatly reduced, owing to the strengthening of the primary film in the early stages, if the higher humidities are approached gradually from zero. At constant relative humidity, just below saturation, time-corrosion curves are convex about the vertical (corrosion) axis; under super-saturated conditions they are concave for about seventy days, when an approximately linear relationship is assumed. This difference is associated with changes in the primary film.

In the presence of traces of sulphur dioxide, when the relative humidity is gradually increased from zero the metal remains bright in the early stages. At approximately 50 per cent. R.H. (the "primary critical humidity") there is a marked increase in weight-increment, followed, at a little higher humidity, by the appearance of rust. At approximately 80 per cent. R.H. (the "secondary critical humidity") there is a still more pronounced increase in the rate of attack, and the specimen becomes rapidly covered with rust. The primary critical humidity probably marks the requisite relationship between water vapour, oxygen and sulphur dioxide

for rusting to commence; the secondary critical humidity depends only on the properties of the initially-formed rust, probably associated with its gel structure, and is independent of the presence of sulphur dioxide.

Differences in the behaviour of iron and zinc under the foregoing conditions are attributed to secondary critical humidity phenomena; at the primary critical humidity the magnitude of the change is practically identical for the two metals, but at the secondary critical humidity the increase in attack, profound for iron, is trifling for zinc. A similar conclusion applies to copper; but whereas the subsequent attack on zinc follows a linear course, that on copper falls off rapidly, the time-corrosion curve flattening toward the time-axis.

Under supersaturated conditions (in presence of traces of sulphur dioxide), during the comparatively short period the specimen is becoming covered with rust, the time-corrosion curve is convex about the corrosion axis (*cf.* "concavity" in purified air for longer periods and much smaller amounts of rust); a linear relationship with time then persists whilst rust accumulates to a thickness several times that of the original thickness of the specimen.

The influence of suspended solid particles has been shown to depend on whether they are (1) intrinsically active, *e.g.*, ammonium sulphate; (2) intrinsically neutral, but capable of adsorbing active gases from the atmosphere, *e.g.*, charcoal; (3) intrinsically neutral, with negligible capacity for adsorption, *e.g.*, silica particles. The "inoculation" of an iron specimen with particles of ammonium sulphate brings about, on exposure to purified air of gradually increasing humidity, primary and secondary critical humidities which, qualitatively, are precisely similar to those induced by traces of sulphur dioxide in the absence of particles. The final attack at 99 per cent. R.H. is much greater under such conditions than when this humidity is maintained at a constant value from the start. This result, the converse of that which obtains in purified air in the absence of particles, is believed to depend partly on the breakdown of the primary film and partly on the influence of the particles on the physical properties of the rust. (In contrast, the corrosion of *zinc* under similar conditions of humidity is very little affected by the presence of ammonium sulphate particles; this, again, is attributed to the almost negligible "secondary critical humidity" in the case of zinc.)

Under supersaturated conditions (purified air) the presence of ammonium sulphate particles on iron greatly increases the rate of attack, particularly in the early stages, the initial convexity about the time axis being replaced by a concavity, or series of concave branches (*cf.* influence of sulphur dioxide). When, however, small amounts of sulphur dioxide are simultaneously present, the influence of this constituent completely masks the influence of particles.

In unsaturated atmospheres, on the other hand, the influence of ammonium sulphate particles is additive to that of sulphur dioxide. Silica particles, which, like charcoal, are without influence in purified air, have only a very slight effect (probably purely mechanical). Charcoal particles have a relatively enormous stimulative effect in the presence of traces of sulphur dioxide, presumably through the local concentration of gas by adsorption.

Carbon dioxide, contrary to the prevailing view, has a marked repressive effect on the corrosion of iron under all conditions investigated, an effect that is attributed to a modification of the gel structure of the primary hydroxide. In supersaturated atmospheres the repressive effect is more marked in the presence of ammonium sulphate particles.

Acknowledgments.

Especial acknowledgment is due to Mr. E. G. Stroud, B.Sc., by whom a large amount of accurate experimental work has been carried out.

The research has been carried out for the Corrosion of Metals Research Committee of the Department of Scientific and Industrial Research, and the author's thanks are due to the Chairman, Professor Sir Harold Carpenter, F.R.S., and to Professor G. T. Morgan, O.B.E., F.R.S., Director of Chemical Research, for facilities afforded and for permission to publish.

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AN ELECTRICAL INVESTIGATION OF SOLUTIONS OF STEARANILIDE IN PARAFFIN WAX.

BY W. JACKSON, D.Sc. AND F. C. FRANK, B.A., B.Sc.

Received 2nd September, 1935.

In a recent paper¹ it was shown that the variation of power factor with temperature and frequency of dilute solutions of cetyl palmitate in paraffin wax is in close agreement with predictions from the Debye theory of dipole orientation. The measurements, extrapolated to zero concentration, gave an apparent dipole moment for the cetyl palmitate molecule of 1.55 D., as compared with 1.78 D. expected from dielectric polarisation measurements on dilute solutions of similar materials in non-polar liquids such as benzene. The present paper describes a series of similar power factor measurements on a dilute solution of stearanilide in a paraffin classed as a 57°-60° C. melting-point wax, itself of negligible power factor, at frequencies from 2.70×10^5 to 1.35×10^7 cycles per second and over the temperature range 0°-80° C. The equipment employed was essentially the same as that described in the preceding paper.

In addition D.C. conductivity measurements have been carried out on this solution over the temperature range 0°-80° C. by means of an equipment that has been described previously.²

Record and Analysis of the Power Factor Measurements.

The curves of Fig. 1 show the variation of the power factor with temperature at each of four approximately constant frequencies, 2.70×10^5 , 1.25×10^6 , 6.10×10^6 and 1.35×10^7 cycles per second, of a 2.68 per cent. (by weight) solution of stearanilide in the wax. It is seen that the power factor increases as the temperature is decreased from 80° C. towards the region of solidification, but that solidification causes a discontinuous decrease at 57° C. for each frequency. It is clear that the peaks of the curves (a), (b) and (c) do not correspond to real power factor maxima, but the curve (d), taken at the highest frequency, appears to pass through such a maximum just previous to the characteristic decrease. It was not possible to make observations during the period immediately following this sudden decrease since the dielectric constant was also changing rapidly, and conditions suitable for measurement

¹ W. Jackson, *Proc. Roy. Soc.*, 1935, **150A**, 197.

² W. Jackson, *Trans. Faraday Soc.*, 1935, **31**, 827.

did not recur until the temperature had fallen to about 52° C. On decreasing the temperature further the power factor was observed to pass through a maximum of relatively low value. The temperature at which this subsidiary maximum occurred was lower the lower the frequency of measurement, an effect in keeping with the theories of dielectric absorption. This applies equally to the region before the commencement of crystallisation.

If the power factor maximum at 60° C. in curve (d), and that at 29° C. in curve (c), be regarded as arising by the Debye mechanism of dipole orientation, deductions can be made of the respective effective dipole moments, and also, the apparent viscosity of the wax at these temperatures being known,¹ of the dimensions of the polar particles present.

Following the same procedure as in the previous paper,¹ the effective dipole moment μ may be calculated from the equation:

$$\tan \delta_{\max.} = \frac{(\epsilon_{\infty} + 2)(\epsilon_0 + 2)}{6\sqrt{\epsilon_0\epsilon_{\infty}}} \cdot \frac{4\pi}{9kT} \cdot \mu^2 n_2 \quad (1)$$

where ϵ_{∞} and ϵ_0 are the dielectric constant values at infinite and zero frequency respectively (for this dilute solution of stearamide these may be taken as equal to the dielectric constant of the wax alone, 2.18, without serious error); k is Boltzmann's constant, 1.37×10^{-16} ; T is the absolute temperature and n_2 is the number of polar molecules in 1 c.c. n_2 is equal to Ncd/M_2 , c being the concentration by weight and M_2 the molecular weight of the solute, d the density of the solution (also taken as that of wax alone), and N Avogadro's number, 6.06×10^{23} .

Corresponding to the power factor maximum of 15.4×10^{-3} , equation (1) gives $\mu = 3.4$ D. for the relevant polar group, while the smaller

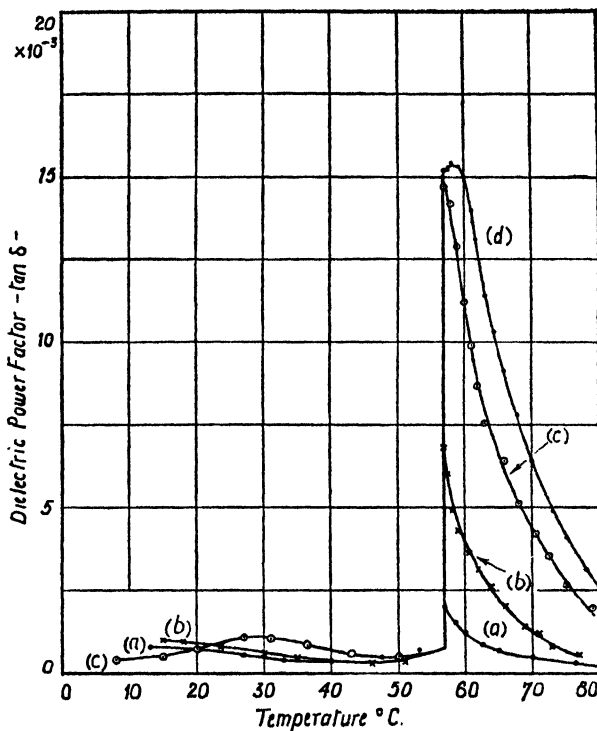


FIG. 1.

Frequencies:—

(a) 2.70×10^6 c.p.s.

(c) 6.10×10^6 c.p.s.

(b) 1.25×10^6 c.p.s.

(d) 1.35×10^7 c.p.s.

maximum, 1.1×10^{-8} , corresponds to an effective moment of 0.9 D. (the molecular concentration being taken in each case as that of the whole of the stearanilide introduced into the wax).

According to the Debye theory, the volume V of the orienting polar group is given in terms of the corresponding values of the viscosity η , the temperature T , and the frequency f at the condition of maximum power factor, by the equation

$$V = kT/6\pi\eta f \text{ c.c.} \quad (2)$$

The viscosity of the molten wax at 60° C. measured directly, is 0.063 poise. The apparent volume of the polar group productive of the power factor maximum at this temperature in curve (a), at 1.37×10^7 cycles per second, is therefore

$$2780 \times 10^{-24} \text{ c.c.}$$

The actual molecular volume of stearanilide, computed from density figures, is about 580×10^{-24} c.c. This suggests the probability that at 60° C., and above, the stearanilide molecules are present in the form of aggregates, especially since volume calculations from relaxation time measurements on simpler molecules have almost invariably given too small a value.

The subsidiary maximum occurs at about 29° C. for a measuring frequency of 6.10×10^6 cycles per second, and, as

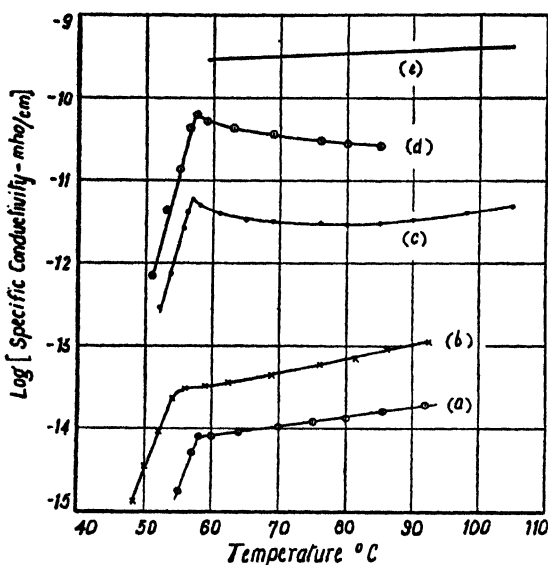


FIG. 2.

- Curve (a) paraffin wax alone.
 (b) 3 per cent. cetyl palmitate solution.
 (c) 2 per cent. stearanilide solution.
 (d) 3 per cent. stearanilide solution.
 (e) variation of fluidity with temperature.

is shown in the discussion below, is probably referable to molecules acting individually rather than as aggregates.

Record of the D.C. Conductivity Measurements.

The D.C. conductivity measurements to be discussed were all made after the voltage had been applied sufficiently long for the residual conducting state to be attained. The curves of Fig. 2 show the logarithm of the specific conductivity of four different paraffin wax solutions plotted against the temperature. Curve (a) relates to the paraffin wax alone, (b) to a 3 per cent. cetyl palmitate solution, and (c) and (d) to 2 and 3 per cent. stearanilide solutions respectively. In each case the curve has been discontinued at a point several degrees below the point of solidification since major interest attaches here to the behaviour in the region of this

change of state. It is seen that the addition of both cetyl palmitate and stearanilide to the wax has been responsible for a marked increase in conductivity, particularly in the latter case. But whereas curve (b) is similar to curve (a) for the wax alone in showing a normal increase in conductivity with temperature, both the stearanilide solutions are anomalous in exhibiting a negative temperature coefficient in the temperature region just above the melting-point. At about 75° C. the temperature coefficient of the 2 per cent. solution commences to reverse in sign, and beyond this temperature the conductivity increases continuously, but at a lower rate than is apparent in the cetyl palmitate solution of curve (b). The temperature coefficient of the 3 per cent. stearanilide solution is still negative at 85° C.

Curve (e) of Fig. 2 shows the variation with temperature of the fluidity of the molten medium as determined by viscometry. The conductivity curves should be parallel to this if the number and size of ions remained independent of temperature.

Interpretation of the Results.

The results of the dielectric loss measurements demand for their interpretation the presence of polar aggregates the volume of which is at least five times the volume of a stearanilide molecule, and probably more since the application of Stokes' law to the calculation of molecular relaxation times commonly fails by a factor of at least ten.^{3, 4}

We are not concerned here with colloidal suspension in the ordinary sense, for the solutions are well below saturation throughout the liquid range studied. We must therefore answer two questions: firstly, are these aggregations to be expected, and secondly, is it to be expected that they should be polar?

Concerning the first question, there is an evident analogy with the results of Ward,⁵ who showed that mixtures of cyclohexane and benzene gave an X-ray diffraction diagram which could be reproduced by superposition of the diagrams for benzene and cyclohexane. This indicates that this solution is of the emulsion type containing local groups of similar molecules. Katzoff⁶ considers that these groups need not be larger than about ten molecules each to account for the results.

In view of this result it seems not at all unreasonable that the anilide molecules in our system should be cybotactically grouped in a similar manner.

Regarding the second question, "Can the aggregates be polar?" reference may be made to another analogy. The properties of the liquid crystal *p*-azoxyanisole are best explained^{7, 8, 9} by the presence of swarms of molecules with their long axes sensibly parallel, but rotating about this axis so that the components of the dipole moments perpendicular to the long axis neutralise each other, while components parallel to this axis are all directed the same way. The swarm has a dipole moment, therefore, of the order n Debye units, where n is the number of molecules in the swarm (the moment of a single molecule is about 2.3 D.). Several different lines of attack indicate that the size of a swarm varies rapidly with temperature, the resultant dipole moment

³ Oncley and Williams, *Physic. Rev.*, 1933, 43, 341.

⁴ W. Ziegler, *Physik. Z.*, 1934, 35, 500.

⁵ H. K. Ward, *J. Chem. Physics*, 1934, 2, 153.

⁶ S. Katzoff, *ibid.*, 851.

⁷ Ornstein and Kast, *Trans. Faraday Soc.*, 1933, 29, 931.

⁸ Kast, *ibid.*, 1064. ⁹ Bernal, *ibid.*, 1067.

being about 10^8 D. near the clearing point (135° C.) and about 2×10^6 D. near the melting-point (116° C.), while the mean volume of a swarm is about 10^{-18} c.c. (i.e. about 10^6 molecules). The relaxation time for swarm orientation changes rather more rapidly with temperature, the critical frequency being 8×10^4 at 118° C. and 2.5×10^6 at 124° C., but the sharpness of the loss curve at any one temperature is sufficient to indicate substantial uniformity of swarm size and the order of magnitude is reasonably compatible with the size of swarm suggested.

The stearanilide molecule satisfies the general criteria for liquid crystal formation;¹⁰ it is a long molecule, having one, and not more than one, "mildly active" group in it. On the other hand the feeble rigidity of the hydrocarbon chain weakens this tendency. Hence though there appears to be no stable liquid crystalline phase of stearanilide, it is by no means surprising that cybotactic groups of stearanilide molecules at temperatures below the melting-point should approximate to such a structure. The interpretation suggested is therefore permissible from this point of view. The aggregates are probably in a state very similar to the swarms of Ornstein and Kast's theory, but their size is the much smaller one characteristic of cybotactic groups in non-crystalline liquids.¹¹

The smaller power factor maximum occurs for a frequency of 6.1×10^6 cycles per second at 29° C., a temperature at which the wax is apparently a solid crystalline network. Reference to the cetyl palmitate solution results¹ indicates that for this latter system at the same frequency the power factor maximum would occur at 26.5° C. This comparison suggests an effective volume for the orienting group in the stearanilide solution 1.5 times as large as for the ester. It appears to correspond, therefore, to single stearanilide molecules. The apparent moment, referred to the total concentration of stearanilide present, is, however, only 0.9 D., whereas the dipole moment of the stearanilide molecule cannot be far from that of acetamide, 3.6 D., so that this reduction must be accounted for. The power loss may be due either to restricted rotation of all the stearanilide molecules present (e.g. about an axis inclined 15° to the dipole axis) or to the relatively free rotation of only a certain fraction of molecules (about $\frac{1}{4}$ th). The first alternative offers a close analogy to *p*-azoxyanisole. In the second case, the molecules contributing to this loss would presumably be those not forming part of swarms.

We must now consider the conductivity phenomena which occur in the same system (Fig. 2). The temperature coefficient of conductivity in the 2 per cent. solution is negative with rising temperature from 57° to 75° C. and anomalously low by comparison with curve (e) from 75° to 85° C. Beyond 85° C. it is anomalously high, i.e. higher than the temperature coefficient of fluidity, although this is the usual phenomenon and merely indicates increasing ionisation or decreasing ion size with increasing temperature. In the 3 per cent. solution the temperature coefficient remains negative up to 85° C. at least. These results suggest an aggregation of charge carriers as the temperature decreases towards the point of solidification.

This aggregation may proceed independently of the aggregation of polar molecules. In this case the conductivity would increase with

¹⁰ J. D. Bernal and D. Crowfoot, *Trans. Faraday Soc.*, 1933, **29**, 1046.

¹¹ Cf. Stewart, *Trans. Faraday Soc.*, 1933, **29**, 982.

falling temperature because the charge on a particle resulting from the aggregation of n ions is increased proportionally to n , while the resistance to its motion increases only in proportion to $3\sqrt{n}$. But the very low total concentration of ions speaks against this independent aggregation. The total concentration may be obtained from Walden's rule in the approximate form,

$$\Delta_0\eta \approx 1.$$

The viscosity of paraffin wax at 80° being 0.0531 and the conductivity of the 2 per cent. solution 2.88×10^{-12} , the approximate molar concentration of ions is about 1.6×10^{-13} . This is only true if their mean radius is about 1 Å. If it is larger the concentration is larger in proportion but even so it can hardly be more than 10^{-12} molar. The primary ions probably arise from impurity in the stearanilide rather than from stearanilide itself. A slight hydrolysis to anilinium stearate is a possibility.

We may provisionally assume that the two processes of aggregation are not independent. Then one species of ion is preferentially adsorbed on the stearanilide aggregates. In detail there are several possibilities, *i.e.* :—

1. Most of the stearanilide molecules are aggregated into groups throughout the temperature range, and these groups grow fewer and larger as the temperature falls. In this case the temperature coefficient of conductivity should be abnormally high so long as most of the groups are free from ions but it can assume a negative value when most groups are charged. This gives much too large values for the group size, for the concentration of stearanilide is about 0.05 molar, *i.e.*, far above the calculated concentration of ions.

2. At the higher temperatures, only a small fraction of the stearanilide molecules are aggregated. Then with falling temperature the number of aggregates will increase rapidly but their mean size only rather slowly. Once more a negative temperature coefficient of conductivity can only be accounted for if the number of ions is not much less than the number of molecular groups, so long as it is assumed constant.

3. If there are still ion pairs present, then their dissociation will be influenced by the adsorption, *i.e.*, it will increase as the adsorbing surface increases. It is only if the stearanilide molecules behave as in case (2) that the adsorbing area increases with fall in temperature. This then seems the most satisfactory explanation of the observed phenomena.

There is some superficial similarity between the effects observed here and those found by Ornstein and Kast⁷ in molten benzophenone and in *p*-azoxyanisole but there is probably no real connection. The explanation given for the latter in terms of its liquid crystal structure seems satisfactory and is inapplicable to our system. The effect in benzophenone may be related, but it extends less than 3° beyond the melting-point.

If the interpretation we have offered for our observations is correct, this system is a very interesting one bordering on three different physical states. The solution is a true solution but of the emulsion type showing a tendency to the clustering of similar molecules. These clusters tend to adsorb ions, assuming a charge, and thus extending the analogy to colloidal systems. And at the same time these clusters may have a liquid crystalline structure.

Summary.

Studies of dielectric loss and D.C. conductivity in dilute solutions of stearamide in molten and solid paraffin wax give results which can only be interpreted by the presence in solution of polar groups of about ten (possibly more) stearamide molecules each. It is suggested that the molecules in the group may approach a liquid crystalline arrangement. The groups also appear capable of adsorbing ionised impurities in the system.

Acknowledgement is due to the Advisory Council of the Department of Scientific and Industrial Research for a grant which made this investigation possible. The work was carried out in the Engineering Laboratory, Oxford.

*The Engineering Laboratory,
Oxford.*

THE REDUCTION OF FERRIC CHLORIDE UNDER THE ACTION OF α -, β - AND γ -RAYS.

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Radon Centre, Barnato Joel Laboratories, The Middlesex Hospital.

Communicated by Professor A. W. PORTER, F.R.S.

Received 23rd September, 1935

In connection with some experiments on another problem, the question arose as to whether ferric iron could be reduced to the ferrous state on bombardment with α -rays. The present investigation was undertaken to decide this, and ferric chloride was chosen as a convenient ferric salt for experiment. Positive results prompted the extension of the experiments to the action of β - and γ -rays.

Preliminary Experiment.

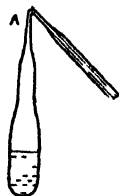


Fig. 1

As a preliminary experiment about 2 c.c. of an almost colourless aqueous solution of ferric chloride were submitted to the radiation from 55.3 mcs. of radon in the bulb shown in Fig. 1. After exhausting and admitting the radon the bulb was sealed at A. On the following day the tube was opened and the residual radon was allowed to diffuse out. Tests on portions of the irradiated solution with potassium sulphocyanide and ammonium hydroxide showed that complete reduction had occurred, while a control solution showed no indication of reduction.

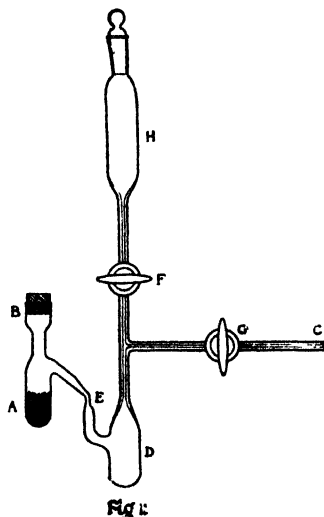
Irradiation of Ferric Chloride in Anhydrous Ether with α -Rays.

In order to see whether the presence of water is necessary for reduction, the experiment was repeated in anhydrous ethereal solution using the apparatus of Fig. 2. The ferric chloride was distilled from A into D and the miniature still was removed at E. Radon, which had been thoroughly

dried over phosphorus pentoxide, was admitted at C, after first exhausting. Anhydrous ether was then run into the bulb D from the funnel, so as to leave a small gas space. The volume of solution was about 2 c.c. and after irradiation with radon, the initial activity of which was 47 mcs., for one week a small, whitish precipitate, presumably of ferrous chloride, was observed. Running in aqueous potassium phosphocyanide from the funnel showed that reduction of the ferric chloride was complete.

Direct Irradiation of Solid Ferric Chloride with Radon.

Since reduction occurs in absence of water, it was decided to irradiate solid anhydrous ferric chloride. In this case it was proposed to estimate the chlorine liberated if reduction occurred. Fig. 3 shows the apparatus used. A light mica vane (Fig. 3a) was suspended from the arm of a torsion balance inside the glass tube (A) by means of a fine platinum wire which passed through the fine orifice (C) without touching the walls of the glass. A continuous current of dry air was passed up through the tube. With



the vane at the position 2, a weighed amount of anhydrous ferric chloride (16.75 mgms.) was distilled on to the vane from the still E. Any crystals of ferric chloride escaping deposition fell to the bottom of the tube B, which was then drawn off in the blowpipe. The vane was lowered to the position 1 and disengaged from the hook on the wire. The whole of the lower part of the tube was detached at G. Radon was admitted over the phosphorus pentoxide J by exhausting, immersing B in liquid air, sealing at N and fracturing a prepared radon tube M by bending at the rubber connection. Finally the radon introducing section was removed at O. The liquid air was removed and the whole was then left for fourteen days. The initial activity of the radon was 103.8 mcs.

At the end of fourteen days, the chlorine liberated was estimated by condensation in the bulb P by immersion in liquid air and subsequent absorption in potassium iodide contained in Q. The liberated iodine was estimated with thiosulphate. The condensation and absorption were repeated to ensure that the whole of the chlorine was accounted for. It was essential that the stopcocks S and T should be lubricated with an inorganic substance which would not absorb chlorine and which would be free from moisture. A metaphosphoric acid in the form of a very viscous liquid was prepared by the British Drug Houses Ltd., and this proved very suitable. Electroscopic tests were made during the irradiation period to ensure that no leakage of radon occurred from the use of this substance, but no leakage occurred.

The total yield of chlorine was found to be 1.002 mgms.

The possible yield from 16.75 mgms. ferric chloride is

$$3.66 \text{ mgms. (assuming that } 2\text{FeCl}_3 = 2\text{FeCl}_2 + \text{Cl}_2\text{).}$$

Hence reduction had again occurred. Although apparently incomplete, it may be that reduction is really complete in the thin layer through which the α -rays penetrate, since they have only a limited range in the ferric chloride. Microscopic examination of the irradiated residue revealed yellowish white portions which may be ferrous chloride.

A small quantity of radon remained when the examination of the contents of the tube was made by condensation in liquid air, and it was neces-

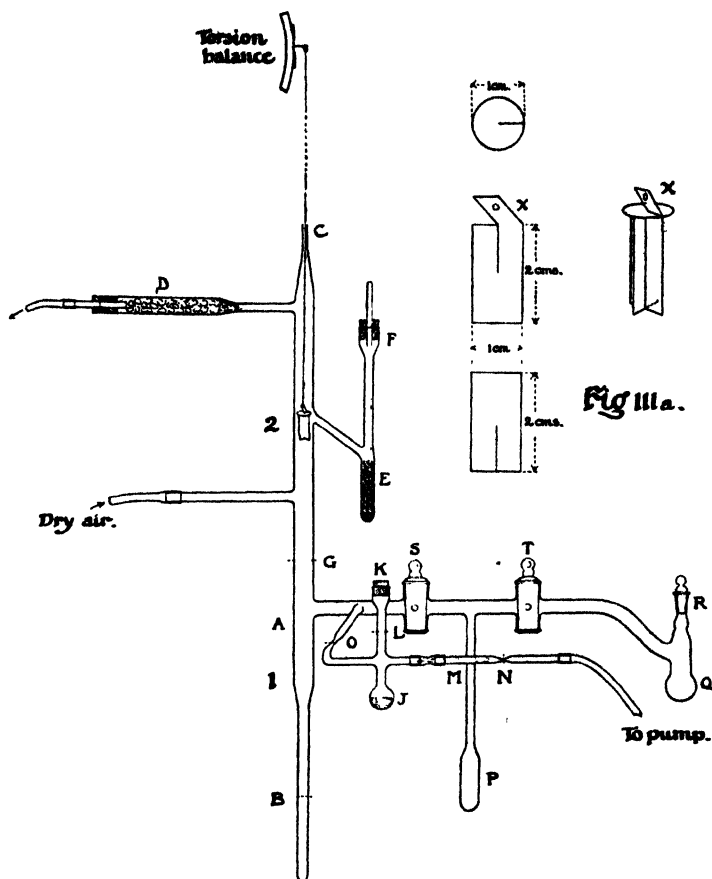


Fig III.

sary, therefore, to ascertain whether the liberation of iodine was due to this residual radon. Using the apparatus of Fig. 4 and imitating as nearly as possible the experimental conditions, potassium iodide was irradiated with radon. Titration with thiosulphate showed the amount of iodine liberated to be quite negligible.

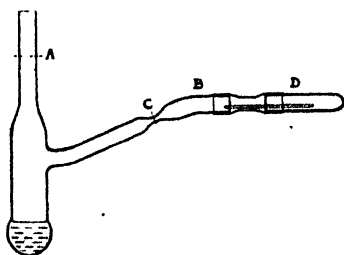


Fig. IV

Irradiation of Ferric Chloride in Aqueous Solution Using β - and γ -Rays.

Having obtained evidence of reduction by α -rays, it was decided to see whether β - and γ -rays were effective also. The source of β - and γ -rays was a thin-walled glass tube containing radon (length 5 cms., diameter 0.75 cms., wall thickness approximately 0.02 cm.) which, while absorbing

α -rays, transmitted a large percentage of β - and γ -rays. Such a tube containing 84.5 mcs. was introduced into the constricted tube D of Fig. 5, which was then sealed at A. 5 c.c. of approximately $N/10$ ferric chloride were introduced through the funnel and were washed down with 2 c.c. of water so as just to cover the radon tube. The funnel was removed and the seal F was made. After exhausting through G, a final seal was made at H. After one week, a titration of the irradiated solution with $N/10$ permanganate gave no indication of reduction.

Irradiation of Anhydrous Ferric Chloride in Anhydrous Ethereal Solution Using β - and γ -Rays.

This experiment was carried out with the apparatus of Fig. 6, which will be seen to be a combination of that shown in Figs. 2 and 5. A radon tube containing 99.5 mcs. was introduced into the reaction vessel E, which was then sealed at A.

After evacuating through C, the seal D was made and a small quantity of anhydrous ferric chloride was distilled *in vacuo* into E from the miniature still, which was then removed in the blow-pipe flame at F. Anhydrous ether was admitted through the tap funnel till the radon tube was covered. A pale yellow solution of ferric chloride was obtained. Examination a few days later showed the yellow colour to be completely discharged, but radiation was allowed to proceed for a total

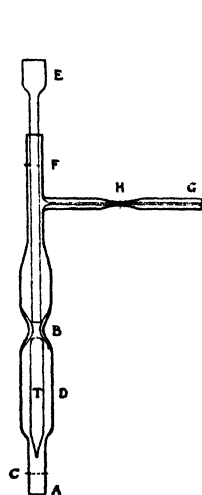


Fig. v.

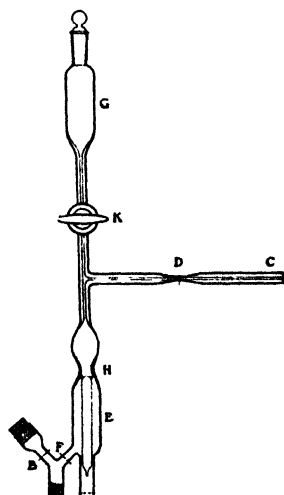


Fig. vi.

time of 1 week. Running in aqueous potassium sulphocyanide showed complete reduction of the ferric chloride.

Repetition of the Irradiation of Aqueous Ferric Chloride with β - and γ -Rays.

When it was found that reduction occurred in ethereal solution and that the case of aqueous ferric chloride using β - and γ -rays seemed to be the only exception to the series of reductions studied, it was thought advisable to repeat the experiment in aqueous solution. A radon tube containing 122.2 mcs. initially was used, and irradiation was allowed to proceed for fourteen days. As before, no reduction could be detected.

Irradiation of more Dilute Aqueous Ferric Chloride, and of Aqueous Ferric Chloride in Presence of Potassium Iodide, Using β - and γ -Rays.

It was thought possible that the reason for the absence of reduction in aqueous solution with β - and γ -rays might be due to a cyclic action whereby

any chlorine liberated from the ferric chloride immediately reacts with the water so as to re-oxidise any ferrous chloride produced. It was thought that the addition of potassium iodide might permit reduction, since any chlorine produced would immediately liberate iodine from the iodide. At the same time it was decided to try the effect of varying the concentration of the ferric chloride by using approximately $N/100$ instead of $N/10$ solution.

Two reaction tubes of the same type as before and as nearly equal as possible were made and two nearly equal β -ray tubes were prepared. To No. 1 vessel was added 5 c.c. of the approximately $N/100$ solution and the β -ray tube had a content of 84.0 mcs. To No. 2 vessel was added 5 c.c. of the solution containing potassium iodide and the radon tube in this case had an initial content of 79.1 mcs.

After one week the two solutions were titrated against approximately $N/100$ permanganate, first extracting with chloroform in the case of the solution containing potassium iodide. While no reduction could be detected in the single ferric chloride solution a small amount of reduction was indicated in the solution containing the iodide, but the unirradiated solution showed reduction to the same small extent. There was, therefore, no evidence of reduction due to the irradiation in either case.

Summary.

The following cases of the irradiation of ferric chloride have been studied:—

- | | |
|------------------------------------|---------------------------------------|
| Using α -rays | (a) Aqueous ferric chloride solution, |
| | (b) Anhydrous ethereal solution, |
| | (c) Solid anhydrous ferric chloride. |
| Using β - and γ -rays | (d) Aqueous ferric chloride solution, |
| | (e) Anhydrous ethereal solution. |

Complete reduction was found to occur in the instances of (a), (b) and (e). In case (c), although reduction occurred it was apparently incomplete, a yield of chlorine 1.002 mgms. being obtained out of a possible total of 3.66 mgms. In this case, too, it is possible that reduction may be complete in the thin layer through which the α -rays penetrate.

In case (d) no reduction could be detected, and this is, therefore, the only exception to reduction in the series studied.

In conclusion I have to thank Professor Russ for suggesting the research and for much help and encouragement during the course of the work; and my thanks are due also to Professor Tuck for his valuable criticism and suggestions.

A FORMULA FOR THE RATE OF EVAPORATION OF ADSORBED ATOMS AND MOLECULES.

By J. K. ROBERTS.

Received 6th August, 1935.

In order to be able to correlate the results of recent experiments on some properties of adsorbed films of hydrogen and oxygen on tungsten,¹ it is necessary to find a formula based on a simple picture of the evaporation of adsorbed atoms or molecules. As the formula is required to cover

¹ See Roberts, *Proc. Roy. Soc., A*, **152**, 445, (1935).

a wide range of types of adsorption it is desirable that the physical significance of the different quantities occurring in it should be clear and that any simplifying assumptions made in deducing it should be explicitly stated.

If there are N molecules per unit volume with a Maxwellian distribution of velocities, the number with velocities between c_0 and ∞ crossing unit area of a given plane in one direction per second is

$$N(2\pi mkT)^{-\frac{1}{2}}(\phi + kT)e^{-\phi/kT}, \quad (1)$$

where $\phi = \frac{1}{2}mc_0^2$ and m = mass of a molecule.

If we are considering the evaporation of light molecules from a solid built up of much heavier atoms, the thermal velocities of the adsorbed molecules will be greater than those of the surface atoms of the solid, and to a first approximation we can assume that the adsorbed molecules are moving in a stationary field of force which is a function of the distance from the solid. We shall consider the particles moving in an outward direction at the part of this field of force where the potential energy is a minimum. The velocity distribution for any given potential energy is Maxwellian, but the density of distribution of particles at different points depends on the shape of the potential distribution curve. If we assume that this shape is similar for all the cases of adsorption with which we have to deal, we may put for N , the volume density of particles which at a given time are at the point of minimum potential energy,

$$N = K'\theta\sigma_1$$

where K' is a constant the same for all adsorbed substances, σ_1 is the total number of places available on unit area of the surface and θ is the fraction of these places that are occupied.

If ϕ is the energy of desorption from the minimum point, only outward moving particles with kinetic energy equal to or greater than ϕ at this point will be able to escape. The number of such particles crossing unit area per second is given by equation (1), and we assume that a fixed fraction of these evaporate. The number $-\sigma_1 d\theta$ evaporating from unit area in time dt is then given by

$$-\sigma_1 d\theta = K''(2\pi mkT)^{-\frac{1}{2}}\phi e^{-\phi/kT}\theta\sigma_1 dt,$$

where we have assumed $\phi \gg kT$, and K'' is another constant. From this it follows that the time t_f required for θ to fall to $f\theta$, where f is a fraction, is given by

$$t_f = -B \cdot \log_{10} f \cdot \frac{(M^{\frac{1}{2}}T^{\frac{1}{2}})}{\Phi} \cdot e^{\phi/RT}. \quad (2)$$

B is a constant the same for all substances, M = molecular weight of adsorbed particles ($O_2 = 32$), and Φ = molecular heat of desorption.²

² The term $e^{\phi/RT}$ necessarily occurs in all formula of this type. Langmuir (*J.A.C.S.*, 1932, 54, 2798), has proposed a desorption formula based on an empirical vapour pressure equation. Polanyi and Wigner (*Z. physik. Chem.*, 1928, 139A, 449), have given a formula for the rate of vaporisation which contains a frequency of oscillation, and some general expression for this would have to be assumed if the formula were to be useful in the present connection. Miyamoto (*Trans. Faraday Soc.*, 1933, 29, 794), has discussed the rate of sublimation but has considered not the number crossing unit area with a given energy but the total number. He has also used a one-dimensional formula—for a discussion of this, see Polanyi and Wigner, *loc. cit.*

The value of the constant B can be obtained from the experimental values given by Langmuir and Villars³ for the rate of evaporation of oxygen atoms from a tungsten filament. The measurements were carried out for low values of θ (from 0.1 to 0.3). The values of t_4 at different temperatures for Φ remaining constant at its value for a sparsely covered surface are: $T = 1856^\circ \text{ K.}$, $t_4 = 1650$ seconds; $T = 1978$, $t_4 = 120$; $T = 2070$, $t_4 = 17.52$. From the ratio of the rates at two temperatures Φ/R can be obtained. Taking the values in pairs 1856/2070, 1856/1978, 1978/2070, we obtain $\Phi/R = 8.27, 7.91, 8.71 \times 10^4$ respectively. The mean is 8.30×10^4 , and thus $\Phi = 165,000$ calories per gram atom, which of course does not differ appreciably from the value 162,000 deduced by Langmuir and Villars from the slope of the log t_4 against $1/T$ curve. Using this value of Φ in the equation for t_f , we obtain a value for B from each measured rate, namely for 1856, 1978, 2070, $B = 2.028, 2.125, 2.028 \times 10^{-13}$ respectively. The mean value of B is 2.06×10^{-13} , so the final formula for t_f is

$$t_f = -2.06 \times 10^{-13} \cdot \log_{10} f \cdot \left(\frac{M^{1/2} T^{1/2}}{\Phi} \right) e^{\Phi/RT}, \quad (3)$$

where t_f is in seconds and Φ in caloric units. It may be noted that the formula now contains no adjustable constant.

The experiments referred to at the beginning of the paper show that the formula is consistent with the behaviour of an atomic film of hydrogen on tungsten of which the heat of adsorption and stability have both been studied. It thus applies with the same constant to an oxygen film which is stable up to nearly 2000° K. with a heat of desorption of 165,000 calories per gram atom and a particle mass of 16, and also to the hydrogen film which is stable up to 600° or 700° K. with a heat of desorption of 59,000 calories per gram atom (this is the initial heat of desorption from a complete film), and a particle mass of 1. The range of atomic films covered accurately is thus very considerable.

The heat of adsorption and stability of a molecular film of oxygen formed by the adsorption of molecules on isolated bare tungsten atoms left during the building up of the atomic film of oxygen⁴ have both been studied. The accuracy of the heat determination in this case was not so high as in that of the hydrogen film, but within the limits of error the behaviour of these isolated adsorbed oxygen molecules is also consistent with the formula. Thus this very different type of adsorption is also covered.

Application to Vapour Pressure.

An indication that the formula may also be applied with reasonable confidence when the masses of adsorbed and solid atoms are not widely different is obtained by considering the case when the two are the same; that is obtaining a general vapour pressure equation based on the above considerations. Langmuir² has shown that the relation between σ_1 the number of atoms per unit area and ρ the solid density is to a first approximation

$$\sigma_1 = 6.43 \times 10^{15} (\rho/M)^{1/2},$$

³ Langmuir and Villars, *J.A.C.S.*, 1931, **53**, 495.

⁴ For a short discussion of how these gaps necessarily occur in the building up of the well-known atomic oxygen film, see Roberts, *Nature*, 1935, **135**, 1037; see also ¹.

where M = molecular weight. Using this, the number of atoms evaporating from unit area per second is

$$C'(2\pi mkT)^{-\frac{1}{2}} \Phi e^{-\phi/RT} \cdot (\rho/M)^{\frac{1}{2}},$$

where C' is the same for all substances. If p is the vapour pressure and if the condensation coefficient is the same for all substances, the number condensing on unit area per second is

$$C''p(2\pi mkT)^{-\frac{1}{2}},$$

where again C'' is the same for all substances. For equilibrium these are equal, from which

$$\log_{10} p = \log_{10} C + \log_{10} A + \frac{2}{3} \log_{10} \frac{\rho}{M} - \frac{A}{2.3RT}, \quad (4)$$

where A the molecular latent heat of vaporisation has been written instead of Φ , and C is a constant.

To test this equation the experimental data collected by Langmuir (*loc. cit.*,² p. 2803) and the values of ρ given in Kaye and Laby's tables have been used. The quantity

$$\left(\log_{10} p - \log_{10} A - \frac{2}{3} \log_{10} \frac{\rho}{M} + \frac{A}{2.3RT} \right)$$

should be the same for all substances. Actually the root mean square deviation from the mean of the values for the seventeen elements included (W is excluded as suggested by Langmuir) is ± 0.33 . This is comparable with ± 0.22 obtained from the same data using Langmuir's vapour pressure formula which is an empirical one. It is considerably better than ± 0.46 obtained from the next best fitting empirical formula quoted by Langmuir.

Summary.

A formula for the rate of evaporation of adsorbed atoms or molecules is obtained directly from simple kinetic considerations. It is consistent with the behaviour of adsorbed films of oxygen and hydrogen atoms on tungsten and also with that of oxygen molecules adsorbed on isolated single tungsten atoms left bare during the formation of the atomic oxygen film. A vapour pressure equation is also deduced.

(Department of Colloid Science,
Cambridge.)

COMPARISON BETWEEN THE EFFECT OF HYDROGEN-ION CONCENTRATION ON THE RATE OF CORROSION OF STEEL IN PURE OXYGEN AND AIR AT 25° C.

By J. M. BRYAN, Ph.D.

Received 13th September, 1935.

The results of a series of experiments on the corrosion of mild steel at 25° C. by solutions of citric acid buffered over the p_H -range 2.4 to 5.5 have already been reported in previous publications.^{1, 2} The factors so far studied have been (1) the effect of surface treatment in the presence

and absence of air, (2) the effect of ferric iron in solution in the presence and absence of air, and (3) the effect of ferrous iron in solution in the presence of air. It was thought that the results for corrosion in the presence of air would be better understood if further studies were carried out to compare its effect with that of pure oxygen over the same p_H -range.

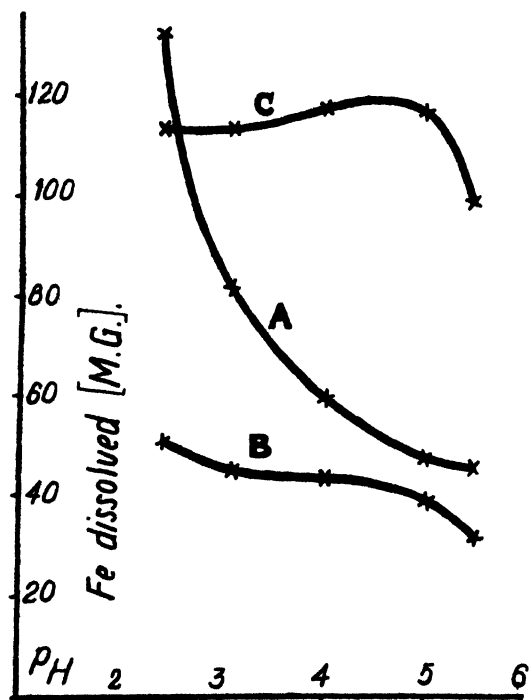


FIG. 1.—Comparison between the effect of H-ion concentration on the rate of corrosion of steel in pure oxygen and air.

- A.—Air present (4 day period).
- B.—Oxygen present (1 day period).
- C.—Oxygen present (3 day period).

The test-pieces, measuring 3 in. × 1 in. and about 1/100th in. in thickness, were abraded with Johnson's "FF" emery cloth, degreased

Methods and Apparatus.

These were in general similar to those described in the previous publications. The sheet of mild steel, from which all the test-pieces were cut, was found to differ somewhat in its behaviour from that used in previous tests, since it corroded faster at high, and slower at low, acidity.

¹ J. M. Bryan, *Trans. Faraday Soc.*, 1933, 29, 1198-1209.

² *Ibid.*, 1934, 30, 1059-1062.

with benzene followed by boiling alcohol, and finally dried in a desiccator before weighing. They were then suspended from glass hooks in the stoppers of the corrosion bottles so that 4 sq. ins. were exposed to the corroding medium. This contained 5 gm. of citric acid per litre of solution, and the hydrogen-ion concentration was varied by buffering with sodium citrate to give the p_H -range 2.41, 3.11, 4.03, 5.04 and 5.54. Each bottle contained 220 c.c. of the corroding medium, and was attached to a gas-burette so that changes in the volume of the gaseous phase during corrosion could be observed. The loss in weight of the test-pieces was taken as a measure of corrosion, and tests were carried out in duplicate to determine (1) the corrosion in the presence of air over a period of four days, (2) the corrosion in the presence of oxygen over a period of twenty-four hours' and (3) the corrosion in the presence of oxygen over a period of three days.

In test No. 1 there were 60 c.c. of gas in the bottles and 10 c.c. in the burettes initially. The solutions were allowed to stand overnight in the thermostatic room at 25°C. in contact with air before introducing the strips. In test No. 2 the volume of gas in the bottles and burettes was the same as in test No. 1, but the solutions were first de-aerated, then saturated with oxygen at 25°C. by allowing them to stand overnight in the thermostatic room in contact with this gas. The saturated solutions were then displaced by means of pressure of oxygen into the corrosion bottles containing the strips, which had been previously exhausted and filled with oxygen. In test No. 3, the conditions were the same as in test No. 2, but the volume of gas in the burettes was 25 c.c. to allow for the greater absorption of oxygen in this test. Gas analyses were carried out at the end of each test.

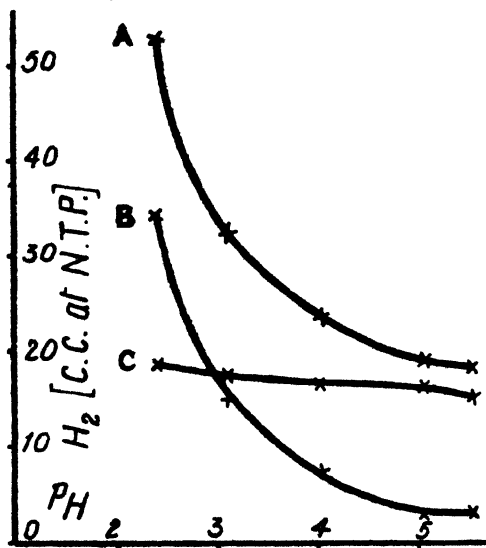


FIG. 2.—An analysis of the reactions for the corrosion of steel in the presence of air at different H-ion concentrations (4 day period).

- A.—Hydrogen-equivalent of iron dissolved.
- B.—Volume of hydrogen evolved.
- C.—Volume of hydrogen depolarised.

Experimental Results.

If we take Curve A of Fig. 1 as typical of the corrosion of a fairly fast-corroding steel, in the presence of a limited supply of oxygen,^a it can be seen that the main effect of a high concentration of oxygen is to mask the effect of hydrogen-ion concentration, and to equalise the rate of corrosion over the greater part of the p_H -range (see Curve C, Fig. 1). At p_H 2.4 the corrosion is much the same in both cases, but the curves diverge greatly from this point towards the more alkaline end of the p_H -range.

The evolution of hydrogen is inhibited by pure oxygen at high acidity (cf. Curves B of Figs. 2 and 4). This is in agreement with previous results

^a T. N. Morris, *Report of the Food Investigation Board for the Year 1931*, p. 184.

with a slow-corroding type of steel in which there was a decrease of the evolution of hydrogen in the presence of air as compared with that which

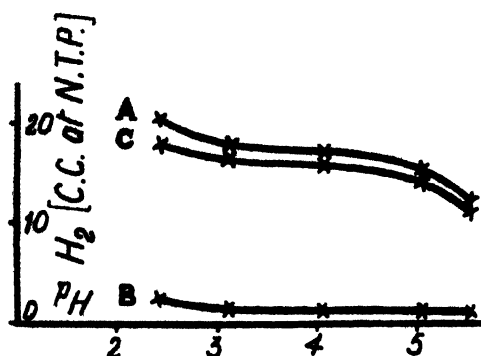


FIG. 3.—An analysis of the reactions for the corrosion of steel in the presence of pure oxygen at different H-ion concentrations (1 day period).

A.—Hydrogen-equivalent of iron dissolved.

B.—Volume of hydrogen evolved.

C.—Volume of hydrogen depolarised.

was entirely due to depolarisation. At high acidity, the total corrosion was not much increased by pure oxygen because the increase in the rate of corrosion through depolarisation was almost counterbalanced by the inhibition of the production of hydrogen already mentioned.

In considering the one-day and three-day tests with pure oxygen (Figs. 3 and 4) we see that, while the curves are of the same general shape, corrosion is greatest for the shorter period at p_H 2.4. After three days, however, there is a maximum at about p_H 4, a fact consistent with previous observations which showed that dissolved iron is most active as an oxygen-carrier for the oxidation type of corrosion at this hydrogen-ion concentration.⁵ It would appear, moreover, in the present tests, that as the concentration of iron in solution increases its effect overshadows that of the

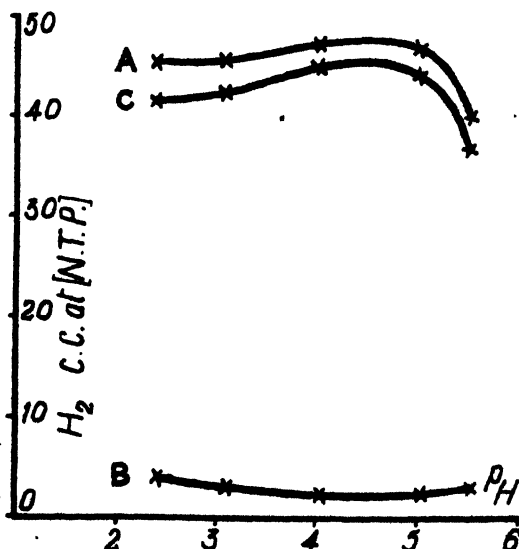


FIG. 4.—An analysis of the reactions for the corrosion of steel in the presence of pure oxygen at different H-ion concentrations (3 day period).

A.—Hydrogen-equivalent of iron dissolved.

B.—Volume of hydrogen evolved.

C.—Volume of hydrogen depolarised.

⁴ *Trans. Faraday Soc.*, 1933, **29**, 1199-1201.

⁵ *Ibid.*, 1934, **30**, 1061.

direct action of oxygen at the surface of the metal, which is greatest initially at high acidity.

Finally, it is of interest to note that in experiments on the corrosion of iron in solutions of potassium chloride, Bengough observed that the evolution of hydrogen appeared to be independent of the oxygen absorption process.⁶ In the present work, however, it has been seen that the evolution of hydrogen was inhibited by a high concentration of oxygen at p_H 2.4, and in previous tests with a slow-corroding type of steel it was stimulated by air at p_H 5.0 to 5.5, as already stated. It is not suggested here that these observations are contradictory to those of Bengough, since the solutions differed both in hydrogen-ion concentration and composition and the result may also have been influenced by differences in the steels used and by other conditions, but it is evident that the subject merits further study.

Thanks are due to Dr. U. R. Evans and Mr. T. N. Morris, M.A., for advice and criticism of this work.

Summary and Discussion.

As this is the end of a series of experiments, it seems desirable to summarise and discuss briefly the scientific facts which emerge from the whole research on the effect of hydrogen-ion concentration on the corrosion of mild steel under apparently static conditions.^{1, 2, 7}

The Effect of Surface Differences.—In general, steel corrodes more readily with a rough than with a relatively smoother surface, because the rougher surface encourages the hydrogen-evolution type of corrosion. In the absence of air the rougher surface stimulates corrosion over the p_H range 2.4-5.5. In the presence of a limited supply of air, the effect is negligible at p_H 2.4, but increases progressively with decreasing acidity to p_H 5.5.

The Effects of Air, Oxygen and Ferric Iron.—Pure oxygen and ferric iron are very similar in their action towards steel, since they both strongly inhibit the evolution of hydrogen at high acidity, and greatly stimulate the oxidation-type of corrosion at low acidity (p_H 5.0-5.5). With air, on the other hand, the inhibition is only slight at high acidity, and there is an actual stimulation of the hydrogen-evolution type of corrosion at low acidity. This stimulation is, however, only an initial effect, and there seems little doubt that it is arrested by an accumulation of dissolved iron, which would tend to prevent free oxygen from reaching the metal. The cause of the stimulation by a low concentration of oxygen is not clear, but it is possible that other factors, such as film formation, have a bearing on the problem. The fact that corrosion is stimulated at low acidity by air and, to a larger extent, by pure oxygen, indicates that the controlling factor in the absence of oxygen is not the rate of deposition of hydrogen ions, but some other factor, probably the overvoltage of hydrogen. Hydrogen-ion concentration appears to be a factor of little importance over the p_H -range when pure oxygen is present, and the rate of corrosion seems to be controlled mainly by either the rate of diffusion of oxygen or its reaction with hydrogen at the surface of the metal. When air is present, the volumes of hydrogen depolarised are also much the same over the p_H -range unless appreciable amounts of dissolved iron are present, but in this case, where the concentration of oxygen is low, a considerable amount of hydrogen escapes oxidation, and is evolved as a gas.

The Effect of Dissolved Iron.—Hydrogen-ion concentration is an important factor in influencing the rate at which dissolved iron oxidises or is reduced. A reduction in hydrogen-ion concentration promotes the oxidation of ferrous iron by oxygen to the ferric condition, whereas an

⁶ G. D. Bengough, *J. Soc. Chem. Ind.*, 1933, **52**, 228.

⁷ J. M. Bryan, *Trans. Faraday Soc.*, 1933, **29**, 830-833.

increase favours the reverse process, *viz.*, the reduction of ferric iron during the evolution of hydrogen. Ferrous iron by acting as an oxygen-carrier in the presence of air promotes the oxidation-type of corrosion over the whole p_H -range; its activity is greatest at about p_H 4. This process becomes increasingly important as corrosion proceeds.

The Appearance of Corroded Specimens.—Specimens corroded above and below p_H 4 show a marked contrast in their appearance when air is present. This is of particular interest, since it provides visible evidence for the transition at p_H 4.3, noted by other workers, between the hydrogen-evolution and the oxidation types of corrosion. The phenomenon is not observed in the absence of oxygen, but the transition is induced by its presence, even in small traces.

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THE ABSORPTION OF DYESTUFFS BY CELLULOSE. PART VI. THE EFFECT OF MODIFICATION OF THE CELLULOSE, AND A THEORY OF THE ELECTROLYTE EFFECT.

BY J. HANSON, S. M. NEALE AND W. A. STRINGFELLOW.

Received 1st October, 1935.

In the preceding papers of this series¹ accurate measurements of the absorption of direct dyestuffs by cellulose were recorded. In them the separate factors involved, such as time of dyeing, temperature, nature of dyestuff and nature and concentration of added electrolyte, were examined in a systematic manner. Most of the experiments were made with a commercial regenerated cellulose sheet prepared by the viscose process, and marketed under the trade name of "Cellophane."

It was therefore desirable to extend certain of the measurements to other forms of cellulose, and in the present communication, data bearing on these points are put forward. Previous knowledge has been almost entirely qualitative, or at most comparative in character, being based upon the visual judgment of those engaged in the dyeing of textiles.

Experimental.

The general technique employed in carrying out the measurements of dyestuff absorption has already been described in the previous papers of this series. It was, however, anticipated that the intensity of stirring would be a much more important factor in working with yarns or fabrics than in experiments on cellophane. The stirring motion whereby the material being dyed is jerked up and down in the solution at the rate of about 100 oscillations per minute was therefore altered so as to permit of a variation of the stroke between one quarter of an inch and three inches.

Experimental Materials.

Dyestuffs.

Sky Blue FF (Colour Index No. 518) was used after thorough purification in the manner already described.

¹ *Trans. Faraday Soc.*, 1933, **29**, 1167; 1934, **30**, 271, 386, 395 and 905.

Cellulose.

(1) **Cotton Cloth.**—A standard bleached cloth made by Messrs. Tootal Broadhurst Lee & Co. Ltd., was used as an example of a carefully purified natural cotton cellulose.

Specification—

Warp 50's Sakel 98 Ends/inch.
Weft 50's Uppers 100 picks/inch.
Copper No (Heyes) 0.04.
Fluidity (in 0.5 per cent. soln.) 4.4.

(2) **"Mercerised" Cotton Cloth.**—The above material was treated with a large excess of 25 per cent. sodium hydroxide solution at 25° C., washed with cold water, dilute acetic acid, and with distilled water until neutral. The material was not constrained in any way, but was allowed to shrink freely during the treatment. This product represents a purified natural cellulose after a process of "swelling" or "activation."¹

(3) **Cotton Cloth after Acid Hydrolysis ("Hydrocellulose").**—The bleached cloth (1) was immersed for 48 hours at 20° C. in a large excess of aqueous sulphuric acid containing 600 grams of acid per litre after the procedure of Birtwell, Clibbens, and Geake.² The product was very thoroughly washed, and dried in the laboratory air. The copper number, determined by the Heyes' micro method, was 3.60, compared with 3.48 obtained by Birtwell, Clibbens, and Geake for their cotton yarn after a similar acid treatment. These authors recorded a loss of 80 per cent. of the tensile strength due to the action of the acid, and a viscosity in 2 per cent. solution 0.095 C.G.S. units. The corresponding fluidity in $\frac{1}{2}$ per cent. solution would be about 40 C.G.S. units.

As may be judged from the great loss of tensile strength, the degree of hydrolysis is much greater than that likely to be encountered in normally processed cotton cellulose.

(4) **Cotton Cloth after Oxidation.**—5 grams of the standard bleached cloth were shaken for 2 hours at 25° C. with 500 c.c. of alkaline hypobromite solution, the solution being tenth normal in free alkali and hundredth normal in oxidising value.³ The product had a copper number of 0.50, and gave a fluidity of 30 in $\frac{1}{2}$ per cent. solution.

Comparing the fluidities of this sample with those of the hydrocelluloses, and taking this quantity as a criterion of reduction in "molecular weight" or chain length, it appears that a similar range of cellulose degradation is represented. The oxidised materials, however, contain a smaller proportion of reducing sugar groups and therefore exhibit lower values of the copper number.

(5) **Cellophane.**—The "300" variety, weighing approximately 2.7 mg. per sq. cm., was used in this work, after washing and sorting as already described. The chemical characteristics of this material were as follows:—

Copper number (Heyes' method) 1.1
Fluidity (in 0.5 per cent. soln.) 10

(6) **Viscose Rayon.**—A sample of Courtauld's filament viscose silk was used in a few experiments. From a chemical point of view, its manufacture and properties are closely similar to the cellophane viscose sheet.

(7) **Cupra Rayon.**—Bernberg $1\frac{1}{2}$ denier filament yarn was used as an example of this material.

¹ Neale, *Trans. Faraday Soc.*, 1933, 29, 228.

² Birtwell Clibbens and Geake, *J. Text. Inst.*, 1926, 17, T145.

³ Clibbens and Ridge, *J. Text. Inst.*, 1927, 18, T135.

Experimental Results.

(1) The Effect of Agitation of the Dyebath upon the Rate of Absorption of Dyestuff.

In quantitative dyeing experiments with cellulose sheet such as have been described in the earlier papers of this series, the rate of absorption of dyestuff is determined by the rate at which dyestuff is supplied to the outer surface of the sheet, and the rate at which the absorbed dyestuff diffuses into the interior. If discs of cellulose sheet are suspended so that they do not touch one another, and if the suspension as a whole is made to oscillate in a vertical direction, it is fairly easy to establish conditions such that the rate at which dyestuff is supplied to the surface is greater than the rate at which it diffuses into the interior of the sheet. The rate of absorption is then determined essentially by the latter process.

When a textile fabric or small hank of yarn is dyed this condition is not attainable with the apparatus now in use. The yarn or fabric is built up of a very large number of intertwined or interlacing hairs or filaments in more or less close contact, with interstitial spaces varying widely in shape and size. Such bodies have, in fact, no definite exterior surface, and in dyeing them the extent of their effective surface will, so far as rate of absorption is concerned, increase as the rate of agitation is increased, and the liquid is thereby forced further and further into the interstices. If, for example, the liquor were forced directly through the fabric a much higher rate of absorption would be anticipated than is observed when the fabric is gently oscillated in the liquor. No change in the magnitude of the ultimate absorption at equilibrium would be expected, however.

The figures given in Table I., which refer to the amount of dyestuff taken up in five minutes at 90° C. from a solution containing 0.05 grams

TABLE I.—EFFECT OF STIRRING UPON RATE OF ABSORPTION.

Vertical oscillations of material in dyebath.
110 cycles per min.

Length of Stroke (inches).	Grams of Dye Absorbed by 100 Grams of Material in Five Minutes.		
	Cellophane (NaCl 20 g./l.).	Cotton Cloth (NaCl 5 g./l.).	Rayon Yarn.
0	0.80	0.090	0.33
$\frac{1}{2}$	0.86	0.142	0.51
$\frac{1}{4}$	0.89	0.186	0.51
1	0.95	0.193	0.53
2	0.97	0.199	0.54
2 $\frac{1}{2}$	—	0.213	0.54
3	—	0.232	0.56

of dye per litre, show the effect of agitation using small pieces of cellophane, or cotton cloth, and very small hanks of rayon yarn as absorbents. The solutions used for the two latter materials contained 5 grams of sodium chloride per litre, but for the cellophane a solution containing more salt (20 grams per litre) was employed so as to increase the relative importance of the stirring by increasing the amount of dye absorbed.

Each figure in Table I. represents the mean of two or more experiments, the differences between

duplicates being much greater when the stirring was inadequate.

In view of the importance of the stirring effect with cotton cloth, and the difficulty of maintaining this factor constant, as well as the impossibility of calculating absolute diffusion coefficients with a material of indefinite shape and surface, it was decided to confine the investigation with cotton and modified cotton to determinations of the amount of dye absorbed at equilibrium. In order to determine the time required for the establishment of equilibrium, samples of the standard cotton cloth were dyed at 90° C. in a solution containing 0.05 grams of Sky Blue FF and 5 grams of sodium chloride per litre; the results are given in Table II.

TABLE II.

		Time (minutes)	5	10	30	
Dye absorbed (gms./100 g. cotton)	(No stirring)		{ 0.093	0.156	0.305	
			{ 0.102	0.168	0.336	
	(Stirred 2" stroke)		{ 0.201	0.283	0.386	
			{ 0.217	0.318	0.406	
		Time (minutes)	60	120	240	300
Dye absorbed (gms./100 g. cotton)	(No stirring)		{ 0.385	0.458	0.465	—
			{ 0.416			
	(Stirred 2" stroke)		{ 0.443	0.474	0.479	0.487
			{ 0.453	0.486	0.478	

It was concluded that experiments carried out with stirring for a period of four hours at 90° C. would give results sufficiently close to the ultimate equilibrium, and this time of dyeing was standardised for the experiments described below.

(2) The Absorption of Dyestuff by Selected Modified Celluloses in Presence of Various Amounts of Added Sodium Chloride.

The values of absorption at equilibrium (four hours' dyeing) expressed as grams of dye per 100 grams of dry cellulose, from a dyebath containing 0.05 grams of Sky Blue FF per litre and maintained at 90° C., are given in Table III. Each value is the mean of two or more measurements. The volume of each dyebath was 150 c.c.; the amounts of "cellulose" dyed ranged between 5 and 60 mgm.

TABLE III.

NaCl, g./l.	Standard Cloth.	Mercurised Cloth.	"Hydro- cellulose."	"Oxy- cellulose."	Cello- phane.	Viscose Rayon.	Cupra Rayon.
0.25	0.060	—	—	0.010	0.034	—	—
0.5	0.100	0.175	—	0.017	0.081	—	0.185
1	0.173	0.275	0.132	0.033	0.215	0.204	0.400
2	0.278	—	—	0.079	0.49	—	0.700
5	0.491	0.750	0.38	0.213	1.12	1.04	1.33
10	0.739	—	0.63	0.427	1.71	—	1.95
20	1.13	1.75	—	0.800	2.6	—	2.94
35	1.57	2.54	—	1.25	3.6	—	—

The absorption by standard cotton from the solution containing 5 grams of salt per litre was checked by an independent technique, in which a relatively very large amount of cotton was used and the fall in concentration of the solution was measured. Two such experiments gave values 0.500, 0.488 (compare 0.491 by the standard stripping method).

Some of the values are plotted in Fig. 1 and the results at low concentrations of salt are plotted on a larger scale in Fig. 2. In order to bring out important differences of shape in this region. In Table IV. the absorption values for the modified celluloses are expressed as ratios relative to the standard cotton.

The following conclusions may be drawn from these results :—

(1) Standard Cotton.

The curve of absorption by standard cotton against salt concentration is not sigmoid as previously found with cellophane, but is convex upwards over the whole range.

TABLE IV.

NaCl, g./l.	Standard Cloth.	Mercerised Cloth.	"Hydro- cellulose."	"Oxy- cellulose."	Cello- phane.	Viscose Rayon.	Cupra Rayon.
0.25	1.0	—	—	0.17	0.57	—	—
0.5	1.0	1.75	—	0.17	0.81	—	1.85
1	1.0	1.58	0.75	0.19	1.23	1.14	2.25
2	1.0	—	—	0.29	1.78	—	2.58
5	1.0	1.55	0.70	0.44	2.29	2.13	2.72
10	1.0	—	0.87	0.59	2.36	—	2.68
20	1.0	1.61	—	0.74	2.37	—	2.68
35	1.0	1.66	—	0.80	2.27	—	—

(ii) Mercerised Cotton.

This material takes up more dye than the standard cotton, in a ratio which is roughly independent of the concentration of salt. This ratio, approximately 1.6 for cloth mercerised without tension and air dried, is closely similar to the ratio (1.5) for absorption of water vapour,² established by Urquhart and Williams.

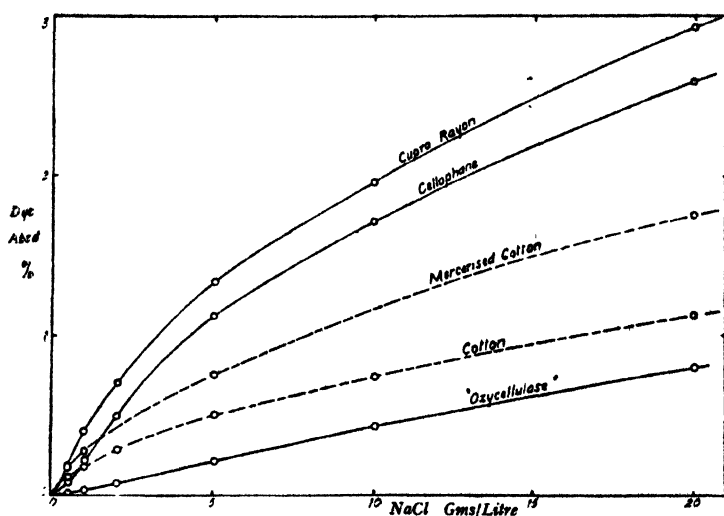


FIG. 1.

(iii) Hydrolysis or Oxidation of the Cotton.

These treatments reduce the absorption. The alkaline hypobromite oxidation is effective in causing a very marked fall in the absorption at low salt concentrations. As the amount of salt in the dyebath is increased, however, the ratio of absorption of oxidised cotton over standard cotton approaches nearer unity.

An examination of Figs. 1 and 2 shows that the absorption-salt concentration curve of the oxycellulose is sigmoid in shape, the absorption at first increasing more rapidly, and then less rapidly than the concentration of salt. The actual figures, over the range 1 to 20 grams per litre, show this very clearly. This sigmoid curve, then, is shown by "cellophane" and by "oxycellulose" but not by the standard cotton. Since the viscose process involves in its earliest stages a considerable oxidation

of the cellulose we may assign the excessive depression of absorption at low salt concentrations—which gives rise to the sigmoid curve—to the oxidation of the cellulose.

(iv) "Cellophane."

The absorption curve previously given for cellophane is confirmed, but the comparison now afforded with the other types of cellulose throws a good deal of light on its shape. Comparing it with the standard cotton cloth, cellophane is a material which has undergone an oxidation of the same order of intensity as the oxycellulose given in the Table, and a swelling treatment considerably more intense than that represented by the mercerised cloth. At low salt concentrations, where, as has already been shown, the depressive effect of oxidation is most marked, the absorption curve for cellophane falls below that for cotton. Above 0.7 grams of salt per litre, however, the effect of swelling predominates, so that from the more heavily dyeing solutions the cellophane takes up more than

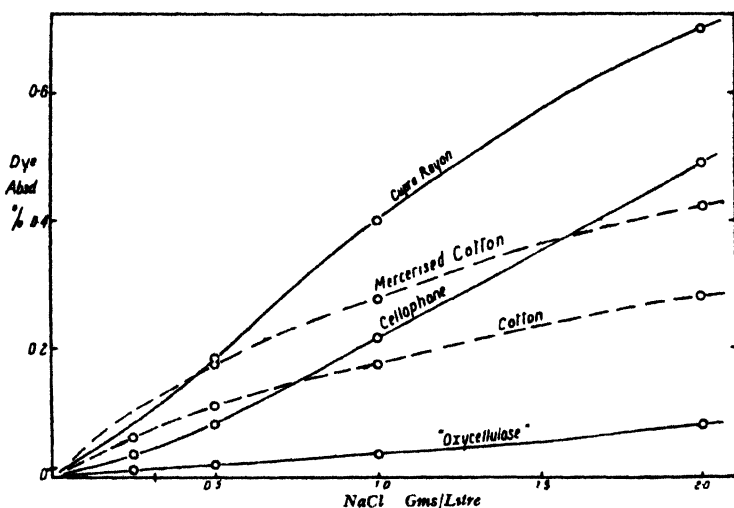


FIG. 2.

twice as much dyestuff as the cotton. This effect is encountered in dye-house practice in the dyeing of mixed fabrics made of viscose and cotton.

The two values given for a commercial viscose yarn are closely similar to those for the cellophane viscose sheet.

(v) "Cupra Rayon."

This material has been prepared from natural cellulose by a process involving dissolution, and therefore, like "cellophane" should show an enhanced absorption compared with natural cotton cellulose. On the other hand, the cuprammonium process of manufacture is not as a rule accompanied by so extensive a degradation of the cellulose (due to oxidation) as is the viscose process. This has been clearly shown by the experiments of Ridge, Parsons and Corner⁵ on the properties of commercial rayons. Bearing these facts in mind, the curve of dyestuff absorption is in line with expectations. The cupra rayon absorbs much more dye than cotton over the whole concentration range, and, comparing the cupra with the viscose rayon, the former, on account of its lower oxidation,

⁵ Ridge, Parsons and Corner, *J. Text. Inst.*, 1931, 22, T117.

shows a higher absorption of dye, more especially at low concentrations of added salt.

Theoretical Discussion.

The Depression of Absorption Consequent upon the Alkaline Oxidation of Cellulose.

Owing to its surprising magnitude, this effect warrants further consideration. A reference to Table IV. shows that the oxidation with alkaline hypobromite reduces the absorption from solutions containing only a moderate excess of sodium chloride to about one-sixth of its normal value. This effect is much greater than would be anticipated from any destruction or inactivation of cellulose sugar residues.

The amount of oxygen consumed in the oxidation is approximately 0.3 grams per 100 grams of cellulose. Assuming that one atom of oxygen completely inactivates one glucose residue so far as absorption of dyestuff is concerned, this amount of oxygen would inactivate only 3 per cent. of the total glucose units. To account for the observed effect on these lines it would therefore be necessary to assume that not more than 4 per cent. of the total glucose units in natural cotton cellulose are accessible to oxidising agents and to dyestuffs. Such a small proportion is highly improbable, at any rate as regards oxidation, and to account for the observed effect we must ascribe an active role to the carboxylic acid groups present in the oxycellulose. A plausible explanation follows from a consideration of the ionic equilibria, and is bound up with the mechanism of the salt effect.

The System Cellulose—Dyestuff—Sodium Chloride—Water. Mechanism of the Salt Effect.

The dyestuff Na_4R is largely ionised in solution, and the anions of the absorbed dyestuff are in some way immobilised by the forces which bring about their absorption. The sodions are not absorbed by cellulose directly, but are concentrated in a cloud near the absorbed anions, so as to maintain approximate electrical neutrality. They tend to escape from this region into the external solution where the concentration of sodions is lower, the free energy change corresponding to the loss of one sodion being

$$RT/N \log a_{\text{Na}_1}/a_{\text{Na}_2},$$

where N is the Avogadro number and a_{Na_1} and a_{Na_2} are the activities of sodion in the concentrated "cloud" and in the external solution respectively. The escaping tendency of the sodions will therefore tend to resist the absorption of dye, according to the magnitude of the factor, $\log(a_{\text{Na}_1}/a_{\text{Na}_2})$. This factor will obviously be diminished by the addition of a neutral sodium salt.

If we make a more or less arbitrary division of the system into two homogeneous phases, cellulose phase and solution phase, the principles of the Donnan equilibrium may conveniently be applied. In the treatment here presented the "cellulose phase," which includes the absorbing surfaces, the absorbed dye anions, the diffusible ions and the solvent within their sphere of influence, is regarded as three-dimensional and a rather arbitrary volume is ascribed to it. It will be apparent, however, that essentially similar relations would still hold good on the

basis of a "two-dimensional" absorbing surface, if it be presumed that the gas laws and therefore the Donnan principle could be applied to the ionic concentrations at the surface, as in the "gaseous" surface films of N. K. Adam.

<i>Cellulose phase.</i>	<i>Solution phase.</i>
(1)	(2)
Cellulose	
Cellulose . . . R ⁻ (adsorbed)	Na ⁺ R ⁻
R ⁻ (free)	Cl ⁻
Na ⁺ Cl ⁻	H ₂ O
H ₂ O	

(The R anion actually carries four negative charges).

The concentration of the cellulose dyestuff complex, *i.e.*, the amount of dyestuff absorbed, should be determined by the concentration of free dyestuff anion. This is determined by the equilibrium between the two phases according to the following approximate relations:—

$$a_{R_1}/a_{R_2} = (a_{Na_1}/a_{Na_2})^4 = \lambda^4, \quad (1)$$

where λ is the ion distribution factor. This equation assumes that Na⁺ and free R⁻ take part in exchange equilibria with the external solution whereas absorbed R⁻ does not.

$$a_{Na_1}/a_{Na_2} = a_{Cl_1}/a_{Cl_2} = \lambda < 1. \quad (2)$$

$$Na_1 = Cl_1 + 4R_1 + 4R_2 \text{ (adsorbed)}. \quad (3)$$

$$Na_2 = Cl_2 + 4R_2. \quad (4)$$

Where Na_1 , Cl_1 , R_1 etc. represent ionic concentrations, the usual square brackets being omitted. R_1 and R_2 are usually small compared with the other three terms.

If there is any appreciable absorption of the dyestuff, a_{Na_1} will be greater than a_{Na_2} , and a_{Cl_1} and a_{R_1} , therefore less than a_{Cl_2} and a_{R_2} , according to equations (1) and (2). The reduction of a_{R_1} below a_{R_2} in the ratio λ^4 , expresses the effect of the escaping tendency of the Na₁ ions, towards a reduction of the amount of dye absorbed. Now if λ (the ratio a_{Na_1}/a_{Na_2}) is made to approach nearer unity, the absorption of dye should increase. This is precisely what happens when sodium chloride is added to the dye-bath, since this increases the Na and Cl terms in equations (3) and (4), relative to the R terms. In other words, the effect of the neutral electrolyte is merely to decrease the inequality of ionic concentrations which originates in the absorption of dyestuff anions by cellulose.

This hypothesis readily explains the striking fact that increasing the concentration of neutral salt may cause a greater increase in the absorption of dyestuff than arises from a proportionate increase in the equilibrium concentration of dye in the solution, since a_{R_1} increases only in direct proportion to a_{R_2} , but in proportion to the fourth power of the ion distribution factor λ .

Deduction of the Equation Relating Absorption to the Concentrations of Dye and Salt.

The fundamental equations given in the preceding section may be used so as to facilitate the calculation of the theoretical variation of absorption with the concentrations of dyestuff and of added electrolyte, in the following manner. Let

d = concentration of dye in solution (gms./litre).

M = Molecular weight of the dyestuff, $Na_m R$.

W = grams of water associated with 100 grams of cotton so as to behave as the solvent in the "cellulose phase" ((1) above).

$x = R_a + R_1$, where R_a and R_1 are the concentrations of bound and free dyestuffs anions respectively, in the cellulose phase.

Then, converting all concentrations into millimoles per 1000 grams of water

$$R_a = \frac{1000d}{M}.$$

$$x = R_a + R_1$$

$$= \frac{D \times 10^6}{MW},$$

where D = absorption of dyestuff (gms./100 g. cellulose).

To obtain a specific solution it is necessary to assume a certain functional relation between R_a , the absorbed dyestuff, and R_1 , the free dyestuff, both expressed in millimoles per 1000 grams of water, in the cellulose phase.

The simplest assumption is that of direct proportionality namely

$$R_a = k' R_1,$$

whence $x = R_a + R_1 = R_1(1 + k') = R_1 k$

(where $k = 1 + k'$).

Assuming the Donnan equation for the distribution of diffusible ions, and writing concentrations for activities we have

$$\left(Na_2 / Na_1 \right)^n = \lambda^n = \frac{R_1}{R_a} = \frac{xM}{1000kd}. \quad (5)$$

also $\frac{Na_1}{Na_2} = \frac{Cl_2}{Cl_1} = \frac{1}{\lambda}$, whence $\frac{Cl_1}{Na_1} = \lambda^2$, approx. (6)

since Na_2 is approximately equal to Cl_2 , R_2 being relatively very small.

Hence $\frac{Cl_1}{Na_1} = \left(\frac{xM}{1000kd} \right)^{\frac{2}{n}}.$ (7)

Also $Na_1 - Cl_1 = nx$ for electric neutrality,

whence $Na_1 = \frac{nx}{1 - \left(\frac{xM}{1000kd} \right)^{\frac{2}{n}}}.$

Substituting now for Na_1 and Cl_1 in the Donnan equation $Na_1 Cl_1 = Na_2 Cl_2$, we obtain

$$\frac{n^2 x^2}{\left[1 - \left(\frac{xM}{1000kd} \right)^{\frac{2}{n}} \right]^2} \cdot \left(\frac{xM}{1000kd} \right)^{\frac{2}{n}} = Na_2 Cl_2. \quad (8)$$

This equation defines x , the equilibrium total concentration of dye in the cellulose phase, in terms of the concentrations of dye and of salt in the dyebath and the absorption constant k .

Test of the Equation using data for the Absorption of Sky Blue FF on Cotton.

Although in the preceding papers of this series a large number of experimental results for the absorption of dyestuffs on viscose sheet have been put forward, none of these are suitable for a simple test of the present theory, since the absorption equilibria are complicated by the ionisation of the carboxylic acid groups present in this oxidised cellulose (see following section). As it is not yet possible to make a quantitative allowance for this effect, the present examination must be confined to the data relating to "standard" purified cotton cellulose.

In the case of Sky Blue FF, $n = 4$ and $M = 992$, so that equation (8) becomes

$$\left[\frac{4x}{1 - \left(\frac{0.992x}{kd} \right)^{\frac{1}{2}}} \right]^2 \left(\frac{0.992x}{kd} \right)^{\frac{1}{2}} = Na_2Cl_2 \quad (9)$$

To evaluate K use is made of the absorption value ($D = 0.491$) at 0.05 g./l. dye, 5.00 g./l. salt. W is assumed* to be 22 (grams per 100 grams cotton) so that

$$x = 45.9D.$$

Substitution of this particular value of x gives

$$k = 3360.$$

Variation of Salt Concentration (Dye = 0.05 grams/litre).

For this case the substitution of $k = 3360$ $d = 0.05$ reduces equation (9) to the form

$$\frac{14.4}{\sqrt{Na_2Cl_2}} x^{\frac{1}{2}} + x^{\frac{1}{2}} - 12.98 = 0. \quad (10)$$

The solution of this equation by successive approximation gives theoretical values for the absorption which are compared with the observed equilibrium values in Table V.

The agreement is very good except at the highest concentration of salt, where, possibly on account of aggregation of the dyestuff, it is always more difficult to reproduce experimental values.

The second column of the table gives the theoretical values of λ , the ionic

distribution factor for the monovalent ions (Na_2/Na_1 or Cl_1/Cl_2). By

TABLE V.

Absorption of Sky Blue FF by Cotton. Dye concn. = 0.05 g./l. Temp. 90° C.

NaCl, g./l.	λ .	$\lambda^{\frac{1}{2}}$.	$D_{\text{calc.}}$	$D_{\text{obs.}}$
0.25	0.356	0.0160	0.059	0.060
0.5	0.405	0.0268	0.099	0.100
1.0	0.460	0.0447	0.165	0.173
2.0	0.520	0.0727	0.268	0.278
5.0	0.604	0.133	(0.491)	0.491
10.0	0.670	0.201	0.742	0.739
20.0	0.745	0.310	1.14	1.13
35.0	0.799	0.407	1.50	1.57

* This value for W is in close agreement with the data of Urquhart and Williams,* for the absorption of water by cotton from saturated vapour at 90° C., but is best regarded at the moment as an arbitrary figure chosen so as to bring theory into the best accord with experiment.

* Urquhart and Williams, *J. Text. Inst.*, 1924, 15, T559.

raising this to the fourth power the values given in the third column are obtained, representing the ionic distribution factor for the tetra-valent dyestuff ions (λ^4). Since the external dyestuff concentration R_2 is a constant, R_1 , and therefore the calculated amount of absorbed dye, are directly proportional to λ^4 .

Variation of Dye Concentration.

(NaCl = 5.00 gms./litre)

The specific equation for this case is obtained by substituting in the general equation (9) $k = 3360$, $Na_2Cl_2 = 7320$,

$$(Na_2 = Cl_2 = 85.5 \text{ millimoles/litre}).$$

Solution by successive approximation gives values which are compared

TABLE VI.

Absorption of Sky Blue FF by cotton at 90° C.
Concn of NaCl 5.00 gm /litre.

Dye, g./l	λ .	λ^4 .	D_{calc}	D_{obs}
0.0095	0.768	0.349	0.245	0.256
0.025	0.672	0.204	0.377	0.376
0.05	0.604	0.133	(0.491)	0.491
0.10	0.538	0.0835	0.617	0.614
0.20	0.476	0.0513	0.757	0.753
0.40	0.420	0.0310	0.915	0.877

with the experimental results, each of which is the mean of at least three determinations, in Table VI.

It therefore appears that the equation which has already been shown to account satisfactorily for the variation of absorption with the concentration of salt, is equally valid when the concentration of dyestuff varies.

The importance of this agreement is emphasised by

the fact that the first set of data cover a 140-fold increase of salt concentration, corresponding to a 25-fold rise of absorption, whilst the second set of data cover a 40-fold increase of dye concentration, which only causes a fourfold increase of absorption.

The present theory takes no account of any aggregation of the dyestuff in solution. The general behaviour of Sky Blue FF suggests that there would be little tendency to aggregate at the temperature used in this work. The experiments of Lenher and Smith⁷ have shown that in presence of moderate amounts of salt aggregation is slight at temperatures near the boiling-point even in the case of Benzopurpurin 4B, which is very much more readily coagulated than Sky Blue FF.

The System "Oxycellulose"—Dyestuff—Sodium Chloride—Water.

This system differs from that in which cellulose is the absorbent, because the "oxycellulose" contains an appreciable proportion of carboxylic acid groups. It has recently been shown⁸ that these groups enter into ionic equilibria with external solutions. Those which are ionised should affect the ionic equilibria in much the same way as an equivalent amount of absorbed dyestuff. The carboxylic acid anion is part of the cellulose structure and, like the absorbed dyestuff anion, is not free to take part in ionic equilibria, whereas the corresponding hydron or sodion is, like the dyestuff sodion, not so restrained, and

⁷ Lenher and Smith, *J. Amer. Chem. Soc.*, 1935, **57**, 504.

⁸ Neale, *Nature*, 1935, **135**, 583.

therefore helps to decrease still further the ion distribution ratio λ . On this hypothesis the ionised carboxylic acid groups should reduce the absorption of dyestuff by an amount of the same order of magnitude as their own concentration.

With this possibility in view the values of absorption by cotton and by "oxycellulose," given in Table III., may be compared again.

Concn. of NaCl (g.l.)	0.25	0.5	1	2	5	10	20	35
Dye absd.								
Standard cotton .	0.060	0.100	0.173	0.278	0.491	0.739	1.13	1.57
"Oxy-cellulose" .	0.010	0.017	0.033	0.079	0.213	0.427	0.80	1.25
Difference .	0.050	0.083	0.140	0.199	0.278	0.312	0.33	0.32

As soon as the absorption of standard cotton exceeds 0.5 the depression due to the oxidation becomes approximately constant, and is equal to 0.3 grams of dye per 100 grams of cellulose, or 1.2 milliequivalents per 100 grams of cellulose (equiv. wt. of Sky Blue FF. = 248).

If it is supposed that the oxygen consumed in the oxidation (approximately 0.3 grams per 100 grams of cellulose) is wholly employed in the oxidation of $-\text{CH}_2\text{OH}$ to $-\text{COOH}$, the proportion of the latter produced would be 9.4 milliequivalents per 100 grams. A provisional estimation by titration with alkali gave 6 milliequivalents of COOH per 100 grams.

To account for the observed depression of dyestuff absorption it would therefore be necessary to suppose that about one-sixth of the carboxylic acid groups were ionised under the conditions of experiment.

It would further appear that the effect of the carboxylic acid groups should increase with the p_{H} of the solution, since this will affect the equilibrium between free carboxylic acid and sodium salt, and

consequently increase the concentration of positive ions within the internal phase. A series of experiments were therefore carried out in which the standard cotton and the oxycellulose previously described were dyed to equilibrium in dyebaths whose p_{H} was varied by the addition of very small amounts of caustic soda or hydrochloric acid. The results are shown in Fig. 3 in which the percentage variation of absorption is plotted against the p_{H} of the dyebath, as measured by the glass electrode at

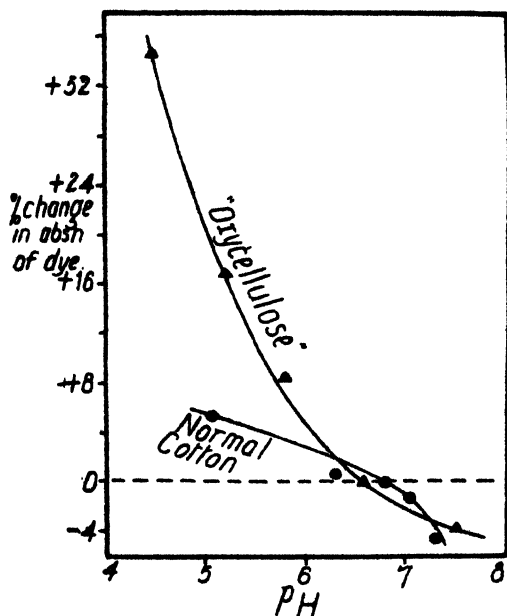


FIG. 3.

room temperature after the absorption had taken place. It will be seen that the theoretical prediction is verified. (The p_H of the normal "neutral" dyebath was found to be fairly stable at about 6.8).

It is hoped to return to this point, and to examine further the quantitative implications of the theory of the salt effect in a further communication.

It is noteworthy that alkaline oxidation—resulting in the formation of the acidic type of "oxycellulose"—is the only kind of cellulose modification which has been found in textile finishing practice seriously to reduce the affinity for direct dyestuffs.*

Summary.

1. Increased motion of the absorbent relative to the dyebath has a profound effect on the rate of absorption of dye by yarns or fabrics. In the case of cellulose sheet the effect of stirring is much smaller.

2. Cellulose which has been swollen (as in mercerisation) takes up more dyestuff than natural cotton cellulose, in a ratio which is unaffected by the concentration of added sodium chloride.

3. Oxidation of cellulose reduces the subsequent absorption of dye, and the reduction is relatively more pronounced at low concentrations of salt.

4. It is suggested that the action of electrolytes in facilitating the dyeing process and also the effect of oxidation in opposing it, arise from ionic equilibria of the Donnan type.

5. Assuming that the dyestuff anion is absorbed by cellulose, an equation relating the absorption to the concentrations of salt and of dyestuff has been deduced on purely theoretical grounds and has been found to account satisfactorily for the experimental results.

6. An extension of the theory taking into account the ionisation of the carboxylic acid groups in "oxycellulose," has been shown to be in qualitative agreement with the facts.

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* Birtwell Clibbens and Ridge, *J. Text. Inst.*, 1925, 16, T52.

ON ADSORPTION PROBLEMS.

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In a thesis (Berlin University, 1924) of which only a small abstract was published in the *Chemikerzeitung*,¹ Kieke described the results of some stalagmometric measurements on the capacity of adsorption of some surface-active and interface-active fatty acids by different organic substances which are insoluble or nearly insoluble in water. The results in Table I. may serve as an introduction to the present work.

The drop numbers of a 1/320 N caprylic acid solution in water at different dilutions were first determined and, from these, the relations between the drop numbers and the concentrations of these solutions could be determined graphically and, if desired useful, by the isotherms. It

¹ A. Kieke, *Chem. Z.*, 1924, 109 and 114.

will suffice here to mention only the drop numbers. As Table I. shows, the substances were investigated in two degrees of dispersion, two sieves being used of 0.07 mm. and 0.3 mm. mesh respectively.

The stalagmometric drop number was 44.5 for water at 15° C. and 80.5 for the 1/320 *N* caprylic acid solution. Three gm. of the solid substance were shaken with 15 c.c. of the acid solution; the drop numbers after the adsorption are shown in Table I.

TABLE I.

	Mesh, 0.07 mm.	Mesh, 0.3 mm.
Anthracene .	53.3	70.1
Carbazole .	66.4	72.6
Phenanthrene .	60.5	66.4
Diphenylamine .	76.1	77.2
Naphthalene .	76.8	78.0
Azobenzene .	78.1	79.2
Acetanilide .	79.5	80.4
Naphthylamine .	80.7	81.6
Salicylic acid .	82.6	83.8

The greatest adsorption is observed with anthracene, carbazole and phenanthrene which are substances of very low solubility in water, scarcely wetted by water. Diphenylamine, naphthalene and azobenzene are wetted to a greater extent, are slightly more soluble in water and are found to be less adsorbed. Acetanilide, naphthylamine and salicylic acid, which are still more readily wetted and more soluble, do not adsorb the acid, or absorbing little. Wetting power, solubility and adsorption are very closely connected.

Table II. contains the results with oleic acid. The drop number for water was 37.8, and for 0.001 *N* oleic acid,* 69.7. Three gm. of the solid substance were added to 15 c.c. of the 0.001 *N* acid and, after adsorption, the unadsorbed acid in the solution was determined stalagmometrically.*

TABLE II.

	Mesh, 0.07 mm.	Mesh, 0.18 mm.
Anthracene .	37.95	39.8
Carbazole .	40.5	43.4
Diphenylamine .	46.3	48.2
Naphthalene .	54.1	55.3
Acetanilide .	58.6	59.1
Naphthylamine .	69.5	69.9
Salicylic acid .	71.7	72.3

The results of Table II. agree with those of Table I. Anthracene has completely removed the oleic acid from the solution, then follow, in order, carbazole, diphenylamine, naphthalene and acetanilide. Naphthylamine and salicylic acid do not adsorb oleic acid under these conditions.

These previous investigations of my co-workers Kieke and Bartsch were continued now in other directions.

1. Results with Aqueous Solutions.

Anthracene, naphthalene, diphenylamine, acetanilide, and phthalic acid were each sieved at room temperature to obtain a uniform dispersion

Octyl Alcohol.	Drop Number.	Caprylic Acid.	Drop Number.
Saturated (approx. 1/320 normal)	100.7 98.8 99.0	0.003 <i>N</i>	90.7 90.1
1/2 saturated	84.85	0.002 <i>N</i>	79.3
1/3 saturated	68.55	0.0015 <i>N</i>	73.7
1/4 saturated	58.45	0.00075 <i>N</i>	63.0
Water	51.5 51.3	0.000375 <i>N</i>	56.2
		water	51.4

* Measured after saponification with potassium hydroxide.

* O. Bartsch, *Kolloid Z.*, 1926, 38, 321.

The portion of each passing through a 0.3 mm. and retained by a 0.2 mm. mesh sieve was used throughout the experiments.

The drop numbers of aqueous solutions of octyl alcohol and caprylic acid were as on previous page.

Anthracene.

A nearly saturated aqueous solution of octyl alcohol was taken which gave drop numbers 98.2, 99.5 and 98.5 (Mean 98.7). Varying quantities of anthracene were shaken with 50 c.c. portions of this solution and the drop number determined in each case. The drop numbers were determined after the filtration. By plotting the results it appears that, under these conditions, 3 gm. anthracene of particle diameter 0.3 mm. adsorb only 0.0075 gm. octyl alcohol from 50 c.c. of almost saturated aqueous octyl alcohol solution. 1 gm. adsorbs therefore only 0.0025 gm.

0.5 gm. anthracene was shaken with 25 c.c. of water and with solutions of octyl alcohol of different concentrations. The following observations were made :—

With 25 c.c. water—no wetting action, no flocculation, 4 c.c. anthracene at the surface.

With 25 c.c. $\frac{1}{2}$ saturated octyl alcohol—4.2 c.c. anthracene flocculated at the surface.

With 25 c.c. $\frac{1}{4}$ saturated octyl alcohol—5.0 c.c. of large flocculate moving to the surface.

With 25 c.c. $\frac{1}{8}$ saturated octyl alcohol—7.0 c.c. of large flocculate, tendency to sink to the bottom.

With 25 c.c. saturated octyl alcohol—9 c.c. very large flocculate at the bottom.

These experiments indicate the interconnection between adsorption and flocculation. The adsorption of octyl alcohol causes aggregation of the anthracene particles to form larger flocculates.

Naphthalene.

The almost saturated aqueous solution of octyl alcohol used had the drop number 96.0.

1 gm. naphthalene + 50 c.c. of this octyl alcohol solution yielded 91.1 drops.

3 gm. naphthalene + 50 c.c. of that octyl alcohol solution yielded 89.4 drops.

From these values we derive a mean corresponding to an adsorption of 0.002 gm. octyl alcohol per 1 gm. naphthalene.

Half gram portions of naphthalene were added to 25 c.c. water and an equal volume of $\frac{1}{2}$, $\frac{1}{4}$, $\frac{1}{8}$, and fully saturated octyl alcohol.

In spite of the adsorption flocculates of different size were not observed in this case, but larger crystal aggregates. The volumes of the crystals linked by octyl alcohol were nearly the same.

Diphenylamine.

1, 2, 3 and 4 gm. portions of diphenylamine were added to an aqueous solution of caprylic acid (nearly 0.0026 normal) which yielded drop numbers of 85.7 and 86.3. The drop numbers of these solutions after adsorption were :—

so that no adsorption has taken place.

When 0.5 gm. diphenylamine were added to 25 c.c. water, or the same

quantity of $\frac{1}{2}$, $\frac{1}{3}$ and fully saturated caprylic acid solution, no flocculates, but only small particles, were formed.

Similar experiments were carried out with diphenylamine and octyl alcohol:—

	Drop Number.
Octyl alcohol alone	89.6 89.45
1 gm. diphenylamine + 25 c.c. octyl alcohol	85.5
2 " " + 25 " "	85.7
3 " " + 25 " "	85.25
4 " " + 25 " "	84.75

These results are very remarkable; in contrast with the results with caprylic acid, adsorption does take place, but it is almost the same for 1 gm., 2 gm., 3 gm.

and 4 gm. diphenylamine. This result is explicable if we suppose that the diphenylamine adsorbs not only the octyl alcohol but also the water, in such quantities, that the concentration of the solution after the adsorption does not change more than corresponds to 0.75 drop.

The experiments opposite with $\frac{1}{2}$ gm. diphenylamine and 25 c.c. of aqueous solution also show that the diphenylamine is flocculated and adsorbed by octyl alcohol:—

	Volume.
With water alone—formation of small particles .	2 c.c.
" $\frac{1}{2}$ saturated octyl alcohol—small flocculates .	3 "
" $\frac{1}{2}$ " " " —somewhat larger .	3 "
" $\frac{1}{2}$ " " " —larger flocculates .	4 "
" fully saturated octyl alcohol—larger flocculates at the bottom	4 $\frac{1}{2}$ "

Acetanilide.

The solution of octyl alcohol employed gave 89.9 and 89.2 drops. There was no adsorption.

	Drop Number.
1 gm. acetanilide + 25 c.c. octyl alcohol	89.4
2 " " + 25 " " "	89.7
3 " " + 25 " " "	88.75

When 0.5 gm. portions of acetanilide were added to 25 c.c. water, $\frac{1}{2}$, $\frac{1}{3}$, $\frac{1}{4}$ and almost saturated octyl alcohol in every case, only

small particles dropping to the bottom of the solution were observed.

Phthalic Acid.

The solution of octyl alcohol employed gave 90.8 and 90.2 drops. There is a small adsorption of the octyl alcohol probably combined with a water adsorption. No flocculation could be observed (see table on next page).

Carbon.

Some experiments with an active charcoal showed that 1 gm. charcoal is sufficient, if mixed with 50 c.c. saturated, octyl alcohol solution to reduce

	Drop Number.	the drop number from 101.1 drops to
1 gm. phthalic acid + 25 c.c. octyl alcohol solution	88.1 88.0	52.4 drops
2 " " " + 25 " " " "	88.3	(drop number of
3 " " " + 25 " " " "	88.15	water 51.4), whilst 1 gm.

non-active charcoal mixed with 50 c.c. of the same octyl alcohol solution reduced the drop number only to 91.4 and 90.6 drops.

2. Results with Emulsions.

The degrees of adsorption mentioned hitherto between the adsorbent and adsorbate were, with the exception of the active carbon, so small that although the surface area of the adsorbent is unknown the Langmuir theory is probably applicable. Not more than one to three layers of the adsorbed substance can be attracted by the adsorbent.

But if we now add to the adsorbent more octyl alcohol or caprylic acid than is soluble in water, the degree of adsorption changes drastically and the Langmuir theory is no longer applicable, for 1000 and more layers can be adsorbed in these cases. Even though an adsorbent such as diphenylamine does not adsorb single molecules (e.g., of caprylic acid) out of an aqueous solution it can adsorb large quantities of that substance, if it is not dissolved in water but in the form of emulsified particles.

It was shown above that 1 gm. anthracene at a degree of dispersion corresponding to a screen of 0.3 mm. mesh if shaken with 50 c.c. nearly saturated octyl alcohol reduces the drop number of the solution from 98.7 drops to 96.2 drops. This reduction corresponds to an adsorption of octyl alcohol not exceeding 0.0017 gm. per 1 gm. of anthracene; we calculated the value 0.0025 gm. per 1 gm. of anthracene.

If, however, one shakes the solution of 50 c.c. of that nearly saturated solution of octyl alcohol with 0.5 c.c. pure octyl alcohol and adds to this milky emulsion 1 gm. of the above anthracene one obtains, after filtration, a solution of octyl alcohol which is nearly clear; the large added quantity of octyl alcohol is nearly completely adsorbed by the anthracene. If one adds instead of 0.5 c.c. not more than 0.2 c.c. of octyl alcohol the filtrate becomes absolutely clear and all the undissolved alcohol is adsorbed. That this adsorption is very stable is proved in the following way. The feebly opalescent filtrate of the mixture 1 gm. anthracene + 0.5 c.c. octyl alcohol + saturated solution of octyl alcohol shows a drop number of 108.6 drops. The anthracene, separated from this solution, was shaken several times with 100 c.c. water and the drop numbers of the successive filtrates were found to be: 98.8; 99.6; 97.5; 99.7; 98.75; 94.5; 88.7; 81.25; 63.2; 52.3; and 51.65; the drop number of the nearly saturated aqueous solution of octyl alcohol being 98.7 and that of water 51.4. These experiments show how firmly the octyl alcohol is held by the anthracene, since no emulsified particles were torn off but only single molecules, to the extent of their solubility in water. We record above that large flocculates were formed by mixing anthracene with solutions of octyl alcohol. The volume of these contained in a mixture of 0.5 gm. anthracene and 25 c.c. of nearly saturated octyl alcohol solution was 9 c.c. If we added 0.1 c.c. of pure octyl alcohol the volume was 14 c.c.; if 0.25 c.c. of octyl alcohol, 9 c.c.; if 0.5 c.c. the floccules became denser and their volume was 3.5 c.c.; and if 1.0 c.c. of octyl alcohol, we obtained a single viscous drop of anthracene + octyl alcohol of 1 c.c. volume and the solution became strongly opalescent.

Doubtless the flocculates are formed by being linked into chains of the anthracene particles and the adsorbed emulsified particles of octyl alcohol; the flocculates, therefore, provide evidence of adsorption. There is in most cases no adsorption, unless flocculates appear. If we shake violently, however, we often obtain a foam consisting of gas bubbles, adsorbent and adsorbate at the surface of the liquid in a connected mass, which, however, separates into single dispersed particles as the bubbles burst and sedimentation proceeds.

These observations are quite general, but the flocculates sometimes present different aspects. It will be remembered that, with 1 gm. of naphthalene, 50 c.c. of saturated octyl alcohol solution reduced the drop number from 96.0 to 91.1 (corresponding to an adsorption of 0.003 gm. per gm. naphthalene). Addition of 0.2 c.c. pure octyl alcohol produced an absolutely clear filtrate and large flocculates, but repeated washing of the naphthalene with water resulted in drop numbers of 81.2; 80.1; 82.4; 83.2; 83.5; 82.0.

In the case of diphenylamine, however, although, *there was no adsorption of caprylic acid, when we added clear solutions of caprylic acid to diphenylamine, when 0.5 gm. of diphenylamine were added to 25 c.c. saturated caprylic acid solution with the addition of 0.2 c.c. of pure caprylic acid, large flocculates were produced.* All the emulsified particles of caprylic acid were adsorbed, although none of the acid dissolved in water was adsorbed. Again from a mixture of 0.5 gm. diphenylamine + 25 c.c. saturated solution + 0.2 c.c. pure octyl alcohol there resulted a clear saturated solution, and all the octyl alcohol not dissolved in water was adsorbed. We observed a large flocculated mass.

With acetanilide there was no flocculation of the sedimenting solid substance and no adsorption when we added $\frac{1}{2}$ gm. acetanilide to 25 c.c. of a saturated solution of octyl alcohol, but if we added 0.2 c.c. pure octyl alcohol, we observed large floccules and all the added octyl alcohol was adsorbed.

With phthalic acid there was a very small adsorption of the dissolved octyl alcohol, but after addition of 0.5 c.c. pure octyl alcohol we got a clear solution and complete adsorption. Only very violent shaking rendered the solution opalescent again. It was to be expected that even an ordinary inactive charcoal would adsorb all the undissolved octyl alcohol. We obtained for 1 gm. of such charcoal and 50 c.c. saturated octyl alcohol (slightly opalescent) the drop numbers 101.3 and 101.0. If we added to those solutions + 0.1; 0.3; 0.6 and 1.2 c.c. of pure octyl alcohol, we obtained drop numbers 106.0; 105.5; 105.0 and 104.4 and after filtration clear solutions and solid carbon which had adsorbed all the undissolved octyl alcohol. *Inactive charcoals are nearly or wholly as efficient as active for the adsorption of emulsified colloidal substances.*

Doubtless a great many inorganic and organic adsorption agents behave in the same manner in respect to many substances in emulsion. See, for instance, the paper on "Benetzungadsorption" by O. Bartsch, *Kolloid-Z.*, 1926, 38, 321, which deals with the adsorption of oleic acid by different mineral substances such as copper pyrites, etc., Bartsch showed microscopically that about 9500 molecular layers of oleic acid were adsorbed on the surface of the mineral. Even though the method is not very exact and the interesting but hypothetical considerations as to the reason of the adsorption are open to question, it is a very remarkable fact that a colloidal substance such as oleic acid is adsorbed by minerals, not in a single layer corresponding to Langmuir's Theory, but in a great many layers. This result of Bartsch is in agreement with my results, which were obtained with organic substances and through a different line of approach.

3. General Results with Colloids.

We have so far considered the adsorption of the larger aggregates of colloid substances, which are emulsified in an aqueous medium containing an organic or inorganic substance with adsorbing qualities. In

these cases the globules of the emulsified substance are generally adsorbed in many layers on the surface of the adsorbing agents.

We may ask, however, what are the adsorbing effects, as the globules become smaller and smaller? Do the above considerations hold for all colloidal particles, submicrons, etc.? In many aqueous solutions of higher alcohols, fatty acids, etc., we have equilibria between molecular and colloidal particles. Are the colloidal particles more readily adsorbed than the molecular particles in such cases? It seems to be so.

According to Gibbs' well-known principle there exists in general a close relationship between the adsorption-capacity of a surface-active substance and its surface activity. In widely different homologous series Traube's rule is equally valid for the surface tension and the adsorption. Traube's quotient approximates to 3.0 for the lower members of a series, but with increasing molecular weight it starts to decrease and finally reaches zero value.³ This effect is caused by the increasing number of colloid particles with increasing molecular weight.

The colloidal particles become adsorbed, but a submicron influences the surface tension very little; if, therefore, a substance dissolved in water contains colloidal particles, *the adsorption on a solid substance will be influenced by both colloidal and non-colloidal particles, but the surface activity is influenced almost exclusively by the non-colloidal particles.*

The close relationship between surface activity and adsorption tends to diminish as the number of more colloidal particles present increase. The adsorption capacity will in these cases be greater than corresponds to the observed surface activity.

H. Freundlich has shown * that in many cases the adsorption of a surface-active substance is much greater than it should be, having regard to its degree of surface activity. Freundlich studied the adsorption of aqueous solutions of surface-active substances by charcoal, and he found that for many aromatic substances the adsorption was much greater than could be expected from the degree of their surface activity. To these groups of substances belong acids such as benzoic and salicylic acid, chlorbenzoic and nitrobenzoic acid, while in the case of the more soluble benzene sulphonic acid (and other acids with sulphonic groups) the capacity of adsorption was much less. Many other substances were strongly adsorbed, many alkaloids and dyestuffs.

Freundlich remarks, that in his experience it was especially the non-volatile substances which showed the most abnormal adsorption. I am convinced that *the principal reason for this phenomenon is the presence, to a greater or less extent, of colloidal particles in those solutions.*

I have measured (with my colleague P. Klein ⁴) a great many Tyndall-ones and have made many ultramicroscopic observations. We found that all the above-mentioned aromatic substances—alkaloids, dyestuffs and many others—which are very strongly adsorbed, contain many colloidal particles. More soluble substances, such as the smaller molecular weight fatty acids and alcohols and other surface-active compounds which do not contain colloid particles show the usual parallelism between surface activity and adsorption.

We remarked at page 240 ⁴: "*Bemerkenswert war die sehr bedeutende Teilchenzahl, welche bei Stoffen der Benzolreihe bei Anilin, Toluidin, Xylidin*

³ I. Traube, *Bföchem. Z.*, 1935, **279**, 173; Chatterji, *Dissert.*, Berlin Technische Hochschule 1933 und Sternglanz, *Z. physik. Chem.*, 1934, A, **169**, 241.

⁴ In his paper: *Über die Adsorption in Lösungen*, *Z. physik. Chem.*, 1907, **57**, 385, and also in his book: *Kapillarchemie*, 1930, I, p. 261.

⁴ Traube and Klein, *Kolloid. Z.*, 1921, **29**, 236.

m-Kresol, etc., beobachtet wurden. Offenbar steht hiermit die starke Adsorptionsfähigkeit aromatischer Stoffe an Kohle, etc., in engstem Zusammenhang." We also showed⁴ that the colloidal particles of the alcohols, fatty acids and halogen alkyls move to interfacial planes to a large extent and that it is there that, in consequence, they have the greatest chance of being adsorbed.

4. The Adsorption of Gelatinous Colloids and Other Considerations.

We know that colloids such as gelatin, albumin, carrageen, etc., are readily adsorbed by many substances. They can displace many other substances from surfaces; an effect which is of importance and well known in the theory and practice of flotation. Such substances are called flotation poisons, since by their affinity to surfaces they displace oil and remove ores from the foam. If added in small quantities to aqueous suspensions of many widely differing substances, they produce by their adsorption a flocculation and accelerated sedimentation: in larger quantities they have dispersing and protective effects on the stability of suspensions. In the first case, when we observe the flocculation and sedimentation of a suspension of any mineral substance (by carrageen, etc.), we see the formation of more or less large flocculates (just as we saw above). The volume of the sediment often becomes much larger, and we can assume that the flocculates here are formed in the same manner. In the one case the surface-active substance (octyl alcohol, etc.) binds together the particles of the adsorbent; in the other the bond is produced by the gelatinous colloids.

We might extend our consideration of the relations between adsorption and flocculation further, but we will only mention that the formation of large flocculates is also observed if an ore such as galena is added to an aqueous solution of an adsorbable organic compound; the flocculates show the adsorption and, in these cases also, very small quantities of the organic substances are sufficient to bind together the particles of ore.

We must mention particularly the flocculation by electrolytes of colloids dissolved in water. Much has been written on this question; it is enough to state here, that the flocculation is always connected with an adsorption of small quantities of ions.⁵

5. The Capacity and Intensity of Adsorption.

In earlier publications I have drawn attention to two components of adsorption energy: *capacity* and *intensity of adsorption*.⁶ An adsorbent can have a large capacity of adsorption, but the intensity of adsorption may be small. In many cases we see that capacity and intensity of adsorption are closely connected.

We have shown above that the emulsified particles of such substances as octyl alcohol and caprylic acid are bound together in such a stable manner with such organic adsorbents as anthracene, that it is not possible, even by repeated washings with water, to separate them from the adsorbents. Applying the same method my colleague Bartsch⁷ has already shown that oleic acid has a large capacity and intensity of adsorption for galena,

⁴ H. Freundlich, *Z. physik. Chem.*, 1903, **44**, 129 and 1910, **73**, 385.

⁶ I. Traube, *Metall und Erz*, 1921, **26**; 1928, **23**; and *Z. angew. Chem.*, 1931, **44**,

⁷ O. Bartsch, *Kolloid. Z.*, 1926, **38**, 326.

copper pyrites, etc., but a small capacity and intensity of adsorption for felspar. Galena adsorbed 99.0 per cent. of oleic acid from 0.001 *M* oleic acid emulsion, and by shaking with water only 2.3 to 0.2 per cent. acid was removed from the galena; felspar adsorbed only 22.0 per cent. of oleic acid under the same conditions, but by shaking with water nearly all the adsorbed acid is very soon freed.

When such volatile substances as chloroform, and carbon disulphide were added in strongly opalescent aqueous emulsions to an adsorbing substance such as anthracene (1 gm. sieved anthracene with 25 c.c. water and 1 c.c. chloroform or carbon disulphide), all the emulsified substance was adsorbed and the aqueous liquid became absolutely clear. We expected a small adsorption intensity, and thought that by washing and shaking the filtered anthracene with water the adsorbed substances might be removed in the form of emulsified globules, but such was not the case. Even if we washed six times with 25 c.c. water we always obtained clear filtrates, and the anthracene had not lost the smell of the adsorbed chloroform and carbon disulphide which are in fact not removed by the water but by evaporation.

My colleague N. Budiloff has measured the intensity of adsorption in an unpublished research,^{*} *Über die Adsorption von Dämpfen durch Kohlen and Silikagel*, by the following method: He first determined by using an U-tube that quantity of the adsorbed substance, in the form of vapour, which is adsorbed by the adsorbent and then led a stream of air through the mass for a number of equal periods. In this way it was shown that substances such as chloroform and carbon disulphide had definitely a larger adsorption capacity than amyl alcohol but the adsorption intensity was much smaller.*

Summary.

1. It is shown that such substances as anthracene, naphthalene, diphenylamine, etc., added to aqueous solution of octyl alcohol and caprylic acid, generally adsorb such small quantities of the adsorbate (a few milligrams per gram adsorbent) that the Langmuir theory may be applicable. In several cases (diphenylamine and caprylic acid; acetanilide and octyl alcohol) the adsorption is practically zero.

2. If these or other adsorbents are added to water-soluble or water-insoluble organic substances in an emulsified state, all the emulsified substances will be adsorbed to a very high degree, even in those cases in which no adsorption takes place for single molecules in clear solution. The adsorption is many hundred times as great as from clear aqueous solution. There are a great many, perhaps several thousand layers of the adsorbate on the surface of the adsorbent.

3. The adsorbate is so firmly held by the adsorbent that washing with water only removes molecular particles, *i.e.*, if they are soluble in water.

4. The well-known parallelism between surface activity and adsorption postulated in Gibbs' principle loses its validity through the presence of colloidal particles in the adsorbate, for in this case the adsorption is larger than corresponds to the surface activity since single molecules diminish the surface tension of an aqueous solution relatively far more than when they are aggregated to submicrons.

5. We found a close relationship between adsorption and flocculation. In most cases adsorption is accompanied by the formation of large floculates of varying volume produced by the linking of the adsorbent particles through the adsorbed substances.

6. A similar relationship between flocculation and adsorption also exists in other cases, *e.g.*, the electrolytic flocculation of colloids by ions, the

* N. Budiloff, *Diplomarbeit, Technische Hochschule Berlin*, 1928.

* For other methods compare my paper: *Über Flotation, Metall und Erz*, 1928, 23, and *Über Adsorptionsintensität und ihre technische Bedeutung, Angew. Chem.*, 1931, 44, 73.

coagulation of organic and inorganic substances by gelatinous colloids, the flocculation of ores by surface active organic substances, etc.

7. Attention is drawn to the two constituents of the adsorption energy *viz.*, the capacity and intensity factors. Methods of determining the adsorption intensity are considered.

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ESTERIFICATION AS A GAS REACTION.

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At present there seems to exist a definite gap between reactions in the gas phase and reactions in solution. The prevalence of ionic mechanisms among reactions in solution exemplifies this fact. An interesting problem arises out of the question whether any typical reactions usually occurring in liquid media can be induced under suitable circumstances to take place in the gas phase, and what under the changed conditions the mechanism will be. For an experimental investigation of this problem the reaction of esterification was chosen. The nature of the results themselves is not such as to make any exact quantitative treatment possible, but the observations are not without interest, and we think should be placed on record.

First the reaction between methyl alcohol vapour and hydrogen chloride was studied. This took place quite readily at an appropriate temperature, and proved to be mainly confined to the surface of the reaction vessel. In this respect it does not differ from many other gas reactions. Although the characteristically erratic behaviour of heterogeneous reactions was in evidence, an approximate quantitative study was possible. The results are briefly summarised in section I.

Next the reaction between methyl alcohol vapour and acetic acid vapour was investigated. This refused to set in with appreciable speed until temperatures were reached at which the decomposition of methyl alcohol made further exploration impossible. There is no great significance in this apparent inertness in the gas phase, since it can be largely accounted for by the much smaller concentration prevailing. This is easily shown by extrapolation of the results found for the esterification of acetic acid in liquid methyl alcohol.

Experiments were then made with the more complex system methyl alcohol vapour, acetic acid vapour and hydrogen chloride. The results were a little unexpected. They were quite unreplicable, and no reaction-time curves could be obtained. Considerable esterification (25 per cent. to 30 per cent.) would occur in a few minutes at 300° C. with the reactants in the proportions of, say, MeOH, 100 mm., HAC, 50 mm. and HCl, 25 mm. Longer reaction times did not increase the amount of esterification significantly. The tendency to esterification increased markedly with the partial pressure of the alcohol, but was rather insensitive to temperature. The conclusion drawn from many experiments was that reaction occurs in an adsorbed layer of alcohol

where ionisation of the catalyst can take place, and that the formation of this layer depends upon uncontrollable factors such as the relative rates of addition of the various reactants, and the exact state of the adsorbing surface. It seems probable that a continuous pool of adsorbed alcohol molecules is necessary: this simulates a two-dimensional liquid, and in it an ionic reaction is possible. It should be mentioned that all parts of the apparatus were kept at such a temperature that no condensation in bulk could occur at any point.

The idea that a continuous array of alcohol molecules was necessary for an effective catalytic reaction led to an investigation of what would happen if, in an alcoholic solution of acetic acid and hydrogen chloride, the alcohol were gradually replaced by a non-ionising solvent such as carbon tetrachloride, which

would not differ very much from a gas phase. The result is rather interesting: there is little falling off in the reaction velocity until the alcohol concentration reaches a quite small value.¹ When the alcohol concentration is still further reduced, the rate of reaction becomes directly proportional to it. The rate is now proportional to the square root of the concentration of the acetic acid, which is present in the form of double molecules. The reaction here begins to show some of the erratic behaviour of a gas reaction. The rate depends upon the size of the liquid-vapour interface, and upon the extent of the glass-liquid interface, though upon neither in any quantitatively exact way. The effect is marked enough, however, to indicate that disturbances in the normal concentrations by

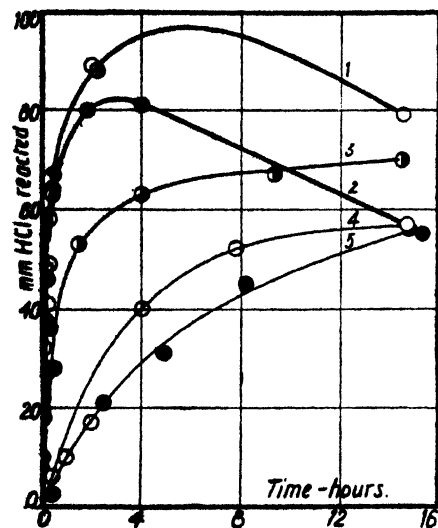


FIG. 1.—Typical reaction-time curves for gas phase esterification of methyl alcohol by hydrogen chloride.

Heavy lines 1 and 2—sphere-packed bulb.

Light lines 3, 4, and 5—unpacked bulb.

Plain circles—200 mm. HCl: 100 mm. MeOH.

Dark circles—100 mm. HCl: 100 mm. MeOH.

Half circles—100 mm. HCl: 200 mm. MeOH.

$T = 1150^{\circ} \text{C.}$

adsorption at interfaces may begin to play a part. To this extent the analogy with the gaseous system is evident. The principal results are given in section 2.

Section 1. Gas Phase Reaction between Methyl Alcohol and Hydrogen Chloride.

The apparatus used was essentially that described in previous papers on the kinetics of gaseous reactions. Since no pressure change accom-

¹ This observation justifies the assumption that in a pure alcohol solution we may take as nearly unity the probability that there is an alcohol molecule present at each collision between the acetic acid and the catalyst, a point to which we would call attention as being of some importance in working out the molecular statistics of this and similar reactions.

pates the reaction, its course was followed by withdrawing samples of the reacting mixture into an evacuated pipette after measured intervals of time, dissolving the samples in water and titrating with standard alkali. The amount of hydrogen chloride used up in the reaction could then be calculated, suitable corrections being applied for the dead space.² Blank tests with hydrogen chloride alone showed the method to be reliable.

The measurements were made at 450° C. Typical reaction-time curves are shown in Fig. 1. From the much increased initial rate in the packed reaction vessel (surface/volume ratio about 16 times that of the unpacked vessel) it is evident that the reaction is heterogeneous to a large extent. The heterogeneous character of the reaction leads to a lack of reproducibility over longer periods of time, though results could be reproduced during a limited series of runs, unless air, or undue excess of alcohol or hydrogen chloride was admitted to the bulb.

The curves in Fig. 1 are best explained by supposing that the initial products are methyl chloride and water. At 450° methyl alcohol itself decomposes only slowly, so that the disappearance of the hydrogen chloride must be due to reaction with the alcohol and not with a decomposition product. The obvious

primary products from this interaction are methyl chloride and water. In the packed reaction vessel methyl chloride itself was found to decompose at the rate of a few millimetres an hour and to yield hydrogen chloride. Thus the slow decomposition of the primarily formed methyl chloride would account for the

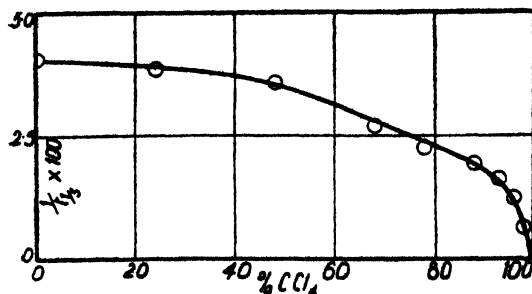


FIG. 3.—Effect of replacing MeOH by CCl₄.

maxima in the curves for the packed vessels. In the later stages of the reaction there are considerable complications, but it is probable that the initial rate represents simply the rate of formation of methyl chloride, unaffected by the slow subsequent decomposition of this substance. Accordingly, the early stages were studied for a series of hydrogen chloride and

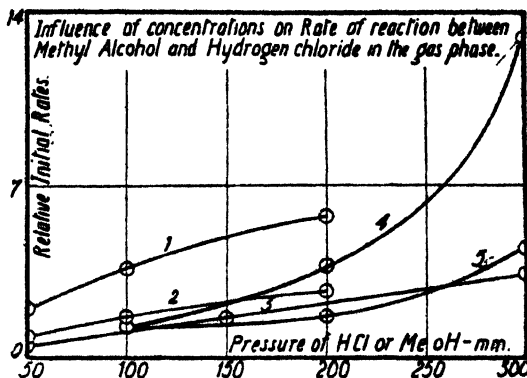


FIG. 2.

Curve 1—variation of rate with HCl.

" 2— " " " HCl.

" 3— " " " MeOH.

" 4— " " " HCl.

" 5— " " " MeOH.

Curves 1, 2 and 3—unpacked bulbs.

Curves 4 and 5.—packed bulbs.

Curves 1 and 2 are for different conditions of surface.

² Cf. *Proc. Roy. Soc.*, 1935, A 149, 340.

alcohol concentrations, and initial rates obtained by drawing tangents to the curves. The influence of the various concentrations on the initial rate is shown in Fig. 2.

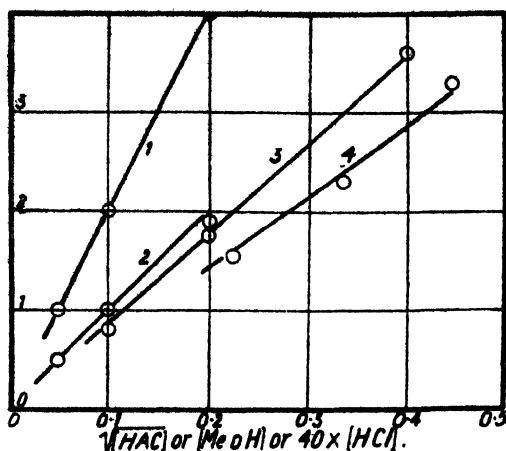


FIG. 4.—Effect of concentration of HAC, MeOH, and HCl on rate of esterification of MeOH by HAC in CCl_4 .

- Curve 1—No CCl_4 —rate $\propto [\text{HAC}]$.
 " 2—In CCl_4 —rate $\propto [\text{MeOH}]$.
 " 3—In CCl_4 —rate $\propto [\text{HCl}]$.
 " 4—In CCl_4 —rate $\propto \sqrt{[\text{HAC}]}$.

gen chloride was generated, dried and passed into a suitable solution of methyl alcohol and carbon tetrachloride, its strength being adjusted by titration and dilution. A specially pure medicinal carbon tetrachloride was used without further treatment.

(a) Effect of Successive Additions of Carbon Tetrachloride to Replace Methyl Alcohol.—The effect of decreasing the alcoholic content is shown in Fig. 3.

The reaction velocity is almost independent of the alcohol concentration until this has been reduced to about one half the original, and even with 95 per cent. carbon tetrachloride the rate is still more than one-third of that in pure alcohol. With more than 95 per cent. carbon tetrachloride, however, a rapid decrease in the rate becomes evident. The rate now becomes proportional to the alcohol concentration, to the hydrogen chloride concentration and to the square root of the acetic acid concentration. (In the absence of carbon tetrachloride the rate is directly proportional to the acetic acid concentration.) These various relations are shown in Fig. 4.

Attempts were made to catalyse this reaction. Nitric oxide and platinum were without influence. Iodine affected the alcohol directly.

Section 2. Esterification of Methyl Alcohol by Acetic Acid in Carbon Tetrachloride Solution, Catalysed by Hydrogen Chloride.

The rate of esterification was followed by alkali titration. The alcohol was dehydrated by the aluminium amalgam method and fractionated, the acetic acid purified by repeated crystallisation. The hydro-

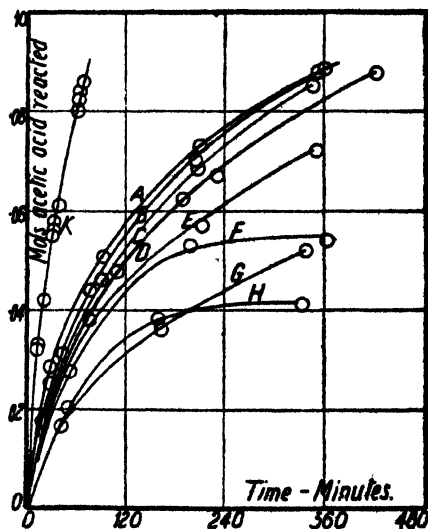


FIG. 5.

gen chloride was generated, dried and passed into a suitable solution of methyl alcohol and carbon tetrachloride, its strength being adjusted by titration and dilution. A specially pure medicinal carbon tetrachloride was used without further treatment.

The measurements upon which the above statements are based were all made in the same type of vessel, and under these circumstances very satisfactorily reproducible results could be obtained, and fresh solutions made up from time to time gave concordant results. When the type of vessel was changed, however, the rate of reaction varied in such a way as to indicate that the areas of the various interfaces were playing a part. This phenomenon is illustrated in Fig. 5. The concentrations employed were: acetic acid 0.20 *N*, methyl alcohol 0.20 *N* and hydrogen chloride 0.005 *N*. For comparison a series of experiments with 20 per cent. alcohol are shown in the figure. For all the vessels the results for the 20 per cent. alcohol solutions lie on curve K, as would be expected from the homogeneous nature of the reaction. The tendency of the reaction in carbon tetrachloride to exhibit some of the characteristics of a heterogeneous gas reaction is evident from the scattering of the remaining curves A-H. These relate to the following conditions:—

A. Glass beads (150 grms.) below the surface of the liquid: liquid-vapour surface, 40 sq. cm.

B. Glass beads (150 grms.) rising above the surface of the liquid.

C. No beads added to flask: liquid-vapour surface, 40 sq. cm.

D. Liquid-vapour surface, 4 sq. cm.

E. Liquid-vapour surface, 1 sq. cm.

F. Liquid-vapour surface, 12 sq. mm.

G and H represent the course of the reaction in two sealed bulbs. In G the bulb was so placed that the liquid surface had an area of 4 sq. cm., while in H the bulb was inverted so that the liquid surface was in a narrow neck of area 12 sq. mm.

It must be noted that methyl acetate could escape by evaporation more readily from the solutions with the larger gas-solution interfaces, and, if methyl acetate exerts a retarding influence on the reaction, then some of the above results would be partly accounted for. But this effect would not be expected to show in the initial stages, and it seems from the figure that the surface affects the initial rate.

While the interpretation of this effect must be given with reserve, there seems little doubt that the contrast between the behaviour in the 20 per cent. alcoholic solutions and in the carbon tetrachloride solutions is real, and we are placing it on record as being of qualitative interest.

Oxford.

THE VAPOUR PRESSURES OF SOME ALKYL SULPHIDES.

BY H. W. THOMPSON AND J. W. LINNETT.

Received 29th October, 1935.

In connection with certain spectral measurements it was recently desirable to know the vapour pressures of some thioethers and mercaptans over a wide range of temperature. Comparatively meagre data exist on this subject, the most important of which were obtained by Berthoud and Brum,¹ who determined the vapour pressures of methyl and ethyl mercaptan, and of dimethyl and diethyl sulphides, at different temperatures, mainly above the boiling-points. In the first three cases the data appear to be fairly reliable, but there are reasons as explained below,

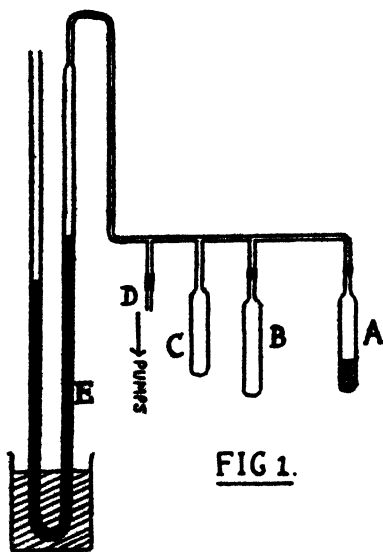
¹ *J. Chim. physique*, 1924, 21, 143.

or doubting the accuracy of the measurements with diethyl sulphide. The determination of the plot of $\log p$ against $1/T$ provides moreover a method of determining the boiling-point of a liquid. It was therefore valuable in our work for checking the boiling-points and testing the purity of small quantities of the purified products too small in quantity to make a conventional determination of boiling-point possible.

We have re-determined the vapour pressure curves of ethyl mercaptan, dimethyl sulphide, diethyl sulphide and measured in addition that of methyl ethyl sulphide. From the data obtained some conclusions may be drawn in regard to molecular association. This is discussed below in relation to the data for the corresponding oxygen compounds.

Experimental Method.

The ethyl mercaptan and thioethers were British Drug Houses products, which by comparison before and after repurification, appeared to



be fairly pure. The thioethers were repurified, first by refluxing over copper powder for 8 hours,¹ then distilling with fractionating column, and finally fractionating *in vacuo* into three or four fractions, the middle fractions being taken. The ethyl mercaptan was fractionated twice *in vacuo*. For the measurement of the vapour pressures the apparatus was that of Fig. 1. The U-tube mercury manometer E had an internal bore of ca. 11 mm., was attached at one end to the tubes A, B, and C, and the exit D, A, B, and D were each separated from the body of the apparatus by a constriction. The repurified product was first solidified by liquid air in A, the apparatus evacuated through D by an oil pump and sealed off. One-third of the liquid in A was then distilled into B and the latter then sealed off. A second (middle) fraction

was then distilled into C and A then sealed off. C was then successively immersed in baths at different fixed temperatures. The levels of the meniscus in E were read off on a cathetometer reading to tenths of a mm. In this way the use of taps was avoided. With the substance in C immersed in liquid air, the difference in levels of the manometer was taken as the barometric height. This was checked at intervals.

The most important baths used were: melting glacial acetic acid, melting ice, melting benzene, mixtures of ice and salt down to $-20^{\circ}\text{C}.$, ice-calcium chloride mixtures down to $-30^{\circ}\text{C}.$ In each case the temperature was checked against a standard thermometer.

Results.

Dimethyl Sulphide: The data are plotted as a $\log p/1/T$ graph in Fig. 2. A satisfactory straight line is found, which when extrapolated

¹ Finkh, *Ber.*, 27, 1239.

backwards gives a boiling-point at 760 mm. of 37.0°C . (*International Critical Tables*, 36.2°C .) The equation of the line is

$$\log_{10} p = -\frac{1505}{T} + 7.734$$

which gives a latent heat of evaporation (λ) of 6910 Cals. The values of Berthoud and Brum give a calculated boiling-point of 36.0°C . and $\lambda=6800$ Cals.

Methyl Ethyl Sulphide: The data are shown in Fig. 2. The calculated boiling-point is 65.0°C . (Beilstein, 65.66°C .) The equation of the line is

$$\log_{10} p = -\frac{1576}{T} + 7.56$$

giving $\lambda = 7250$ Cals. Berthoud and Brum give no data for this compound.

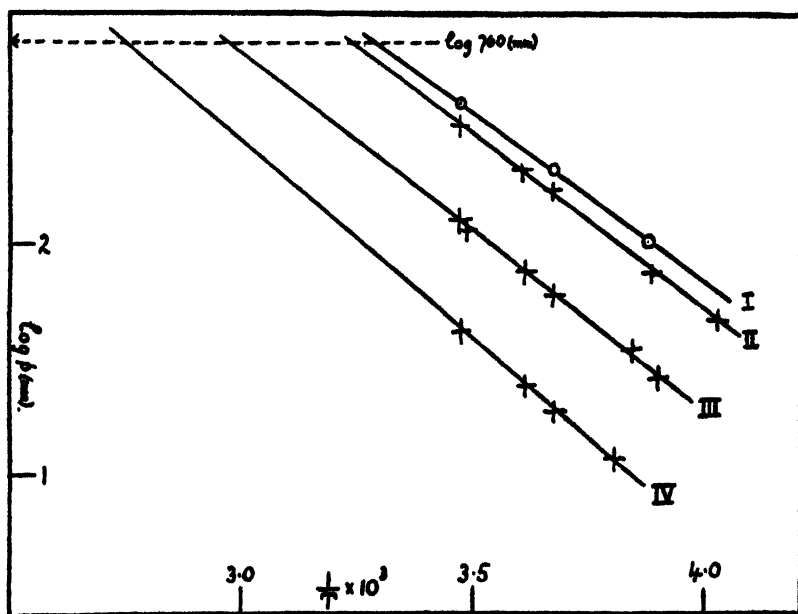


FIG. 2.

- | | |
|----------------------------|-----------------------|
| I Ethyl mercaptan. | II Dimethyl sulphide. |
| III Ethyl methyl sulphide. | IV Diethyl sulphide. |

Diethyl Sulphide: From the data of Fig. 2 the calculated boiling-point is 91.4°C . (*International Critical Tables*, 91.6°C .) The equation of the line is

$$\log_{10} p = -\frac{1740}{T} + 7.65$$

giving $\lambda = 8000$ Cals. The data of Berthoud and Brum give an extrapolated boiling-point of 87.5°C . which seems too low, and their value of λ is 8970 Cals, which seems too high. A further reason for doubting their data is found in connection with their value of the Trouton Constant discussed below.

Ethyl Mercaptan: The data are also plotted in Fig. 2. The extrapolated boiling-point is 33°C . (*International Critical Tables*, 34.7°C .) The

equation of the line is

$$\log_{10} p = -\frac{1492}{T} + 7.76$$

giving $\lambda = 6860$ Cals. Berthoud and Brum's data give $\lambda = 6820$ Cals.

Discussion.

The extent to which alcohols and ethers on the one hand, and thioalcohols and thioethers on the other, are associated in the liquid phase has been recently discussed by Sidgwick.³ From a consideration mainly of the boiling-points of the corresponding oxygen and sulphur derivatives it has been supposed that whereas water and the alcohols are noticeably associated, neither ethers nor any of the sulphur compounds are abnormal.

It has long been known that the value λ/T_b for a normal liquid should be ca. 21.7. Estimates of this Trouton Constant in the present case

TABLE I.

X =	O.	S.
(CH ₃) ₃ X	22.3	22.3
(CH ₃)(C ₂ H ₅)X	22.0	21.4
(C ₂ H ₅) ₂ X	20.2	21.7
(CH ₃)(C ₂ H ₇)X	22.2	—
(C ₂ H ₅)(C ₂ H ₇)X	21.8	—
(C ₂ H ₅) ₂ X	22.9	—
CH ₃ .X.H	25.0 *	22.5
C ₂ H ₅ X.H	26.8 *	22.4
nC ₂ H ₇ XH	26.6 *	—
HXH	26.2 *	21.4

* Indicates abnormal value.

have not apparently been used to test the conclusions just stated. We have evaluated the constant for the various substances with the results opposite. The values for the substances given in Table I. and not studied in the present experimental work are obtained from *International Critical Tables*. It should, however, be observed that the calculation of this constant from the vapour pressure of ethers given in *International Critical Tables* leads to values uniformly somewhat higher than the values given above, which are presumably determined by a different method. The differences are however insignificant for the present purpose. There appears to be a noticeable discrepancy in the case of hydrogen sulphide. The value of λ/T_b given in *International Critical Tables* is 21.4. The vapour pressure data in Landolt-Börnstein, and in the *International Critical Tables*, lead to values 23.7 and 25.5, although the extrapolated boiling-points are approximately correct (-60° C.). It is probable that the vapour pressure data are in error.

It is seen that in general, whilst water and the alcohols have an "abnormal" constant, ethers, thioalcohols and thioethers behave in comparison as normal unassociated liquids, within the limits of accuracy of the values of the constant. It should be remarked that Berthoud and Brum's value of the constant for diethyl sulphide is 24.9, which is clearly in error. * The previous suppositions are therefore confirmed.

³ *The Electronic Theory of Valency*, 1st Edn., pp. 135, 285.

Summary.

The vapour pressures of some alkyl sulphides and ethyl mercaptan have been determined at a series of temperatures below the boiling-point. The values of the Trouton Constant are calculated from the data and inferences drawn in regard to the association of the substances in the liquid state.

We thank the Department of Scientific and Industrial Research for a maintenance grant to one of us (J. W. L.).

*The Old Chemistry Department,
University Museum, Oxford.*

REVIEWS OF BOOKS.

Handbook of Chemistry. Compiled and edited by N. A. LANGE, assisted by G. M. FORKER. (Sandusky, Ohio, 1934: Handbook Publishers Inc., 8vo, pp. xiv and 1266. Price \$6, or to students and teachers \$3 post paid.)

The compilers have carried through a very large task. The completeness of the information may be judged by the tables of physical constants which occupy: inorganic compounds, 111 pages; organic compounds, 234 pages; alkaloids and glucosides, 20 pages. Each pair of facing pages gives particulars of crystalline form and colour, S.G., M.P., B.P. and solubility of some forty substances. Convenient cross-references save duplication of the information in respect of the synonyms of the 4452 organic substances listed. The information is compiled from Mellor, Abegg, Gmelin-Kraut, Friend, Winchell, Comey and Hahn, Seidell, the International Critical Tables, the Tables Annuelles and Beilstein. Space forbids even a summary of the nature of the tables and other information made available in concise form. Suffice it to say that there is little the chemist, chemical engineer or physicist needs which is not to be found. There is appended a mathematical appendix of 248 pages which is published separately and has already been reviewed in these columns.

In spite of the fact that more than 1500 pages are bound in one volume it is not unwieldy, as particular care has been given to the choice of paper and the details of binding. The printing is excellent.

Annual Reports on the Progress of Chemistry for 1934. Volume XXXI. (London: The Chemical Society. Pp. 442. Price 10s. 6d. Postage 6d.)

The familiar binding and excellent get-up, but unfamiliar advertisements! But no admirer of this annual of our colleague Society—and we are all in that class—will carp at this much needed addition to revenue.

As usual the reports are masterpieces of lucidity and summary. The reports on physical chemistry deal, as heretofore, with special topics, it being left to H. W. Thompson to sum up the not inconsiderable residuum of which we ought to be told. The special reports in this section are: Heavy Hydrogen, Electrolytes, Kinetic Salt Effects, Acids and Bases by

R. P. Bell; *The Raman Effect* by L. A. Woodward; *Resonance and the Co-ordination of Hydrogen*, *Heats of Formation in Homologous Series* by N. V. Sidgwick; and *Chemical Kinetics* by E. J. Bowen.

In conclusion mention may be made of the excellent review of recent work on the Corrosion of Metals by E. S. Hedges.

A German-English Dictionary for Chemists. By A. M. PATTERSON. 2nd Edition. (London: Chapman & Hall Ltd., 1935. Pp. xx and 411. Price 15s.)

Those of us who have conducted examinations know what a large following Patterson has had since the first edition was published in 1917. The new edition has 42,000 entries; this involves very many new entries and the deletion of "unlikely" words. By the introduction of fresh additional meanings the dictionary is made even more complete. There has very usefully been incorporated, in the ordinary dictionary entries, the contents of a glossary of terms relating to atomic structure.

The inclusion of commonly occurring abbreviations is a useful feature. We wonder, by the way, who was the bright person who suggested to compilers of English-German dictionaries that Englishmen ever write "f.i." for "for instance"! Germans, however, so frequently abbreviate that we may hope never to be led into such solecisms.

Intermediate Physics. By C. J. SMITH. 2nd edition. (London: Edward Arnold, 1935. Pp. xii and 900. Price 16s.)

Three impressions of the first edition and now, only three years after the first, a second edition! Dr. Smith joins the ranks of "best sellers"; surely an unusual thing in scientific text-book writers. So thoroughly has the book been re-written that it contains 250 more pages than the first edition.

Thorpe's Dictionary of Applied Chemistry. Supplement volume 2 (N—Z). Compiled by J. F. THORPE and M. A. WHITELEY. (London: Longmans Green & Co. Ltd. Pp. xx and 727. Price 60s. net.)

The scheme outlined when the first supplementary volume was brought out has been generously followed in the present volume, but from considerations of space the index is omitted. This, with a glossary, will follow.

A dictionary is not a book for light reading, so the reviewer does not pretend to emulate the industry of the compilers and of Dr. Goldsmith who have read this volume all through with admirable results in the printing and make-up. Nor does the reviewer follow the example of the respectable matron who complained to Dr. Johnson of the omission of swear words. He has looked for and read the parts of which he *ought* to know something and by them he must judge the whole.

Among the articles read are the following: "The Utilisation of Atmospheric Nitrogen," by Professor Partington (a clear and impartial recorder), "Free Radicals," by Dr. T. G. Pearson (free acknowledgement being given

to our recent General Discussion), "The Parachor," by Professor Sugden (who better than its father can know this son), "Spectroscopy," by R. A. Morton (a disciple of Professor Baly), "The Stereochemistry of Cyclic Compounds," by Dr. Mills, "Thermometry," by Ezer Griffiths, "Thermodynamics," by J. C. Swallow of I.C.I., and "Wetting-out Agents," by Ellis Clayton. All are authorities on their subjects.

This supplementary volume is a worthy successor and all who possess the Dictionary will need it to complete the set. Indeed it is to be hoped that many seeing the supplement will purchase the whole. The sole deterrent is, however, the formidable one of hard cash. We cannot say that this dictionary is expensive when we consider the herculean labour involved, but it is certainly not cheap. We seriously wonder whether in the long run it would not be a paying proposition to prepare to sell a large edition at about one-third of the price. If, as we imagine, a complete new edition is a thing of the rather distant future, why not reprint the whole dictionary and supplements to sell at seven or eight pounds complete? A work of this character is not comparable with a specialist book for which a strictly limited sale has to be compensated by a high selling-price. The potentiality of sales is, comparatively speaking, unlimited; every chemist would like to have Thorpe—if only he could afford it.

Cumming and Kay. A Textbook of Quantitative Chemical Analysis.

Sixth Edition, revised by F. C. GUTHRIE and J. T. NANCE. (London: Gurney and Jackson. 1932. Pp. xv and 482. Price 15s. net.)

The most significant testimony to the value of Cumming and Kay is that a sixth edition is now required. The new edition well maintains the standard set up; it incorporates many new features. The chapters on electrolytic methods and on the determination of p_H (written pH) are to some extent re-written. The first chapter on volumetric analysis and the calibration of apparatus has also been revised.

The revisers have "adopted" the millilitre. The reviewer confesses to a conservative hankering after his old friend the c.c.; when the difference in the units assumes more than theoretical importance he is much more likely to express himself in litres than in c.c., or m.l. He is more likely to say 10 litres than 10,000 m.l., so it does not much matter that 10,000 c.c. is just over $\frac{1}{2}$ c.c. wrong. It is doubtless right that the new generation should be brought up properly; one always has the fear, however, that the young worker will see in this an excuse for the common hankering after that fourth or fifth insignificant figure which is perennially perpetuated in automobile records.

Elementary Electrical Engineering. By ALBERT E. CLAYTON and HERBERT J. SHELLEY. Second Edition. (London: Longmans Green. Pages xi and 462. Price 7s. 6d. net.)

Six impressions of the first (1927) edition of this book intended for first and second year students were necessary. The new edition incorporates more recent developments.

The Spirit of Chemistry. By ALEXANDER FINDLAY. Second Edition. (London: Longmans, Green & Co. 1934. Pp. xvi and 510. Price 10s. 6d.)

The first edition of Professor Findlay's readable book was reviewed in these Transactions in 1931. The new edition comprises 30 more pages, but generally continues on the already proved lines.

Probability and Random Errors. By W. N. BOND. (Edward Arnold. Pp. viii and 141. Price 10s. 6d.)

Dr. Bond is always expected to be interesting; he has the teacher's flair for clear exposition and apt illustration, and knows just how much—and how little—knowledge to assume in his readers.

In the present volume he begins at the beginning by devoting a couple of illuminating chapters to the fundamentals of probability. He then proceeds to discuss Types of Error, the Estimation of Errors, the Combination of Observations, Linear Graphs and Correlation, Curve Fitting and Periodic Curves.

The treatment is, at various critical points, illustrated by admirably chosen examples drawn from different branches of the physical sciences. It may be commended to readers who find Whittaker and Robinson rather difficult and, indeed, forms a very useful introduction to that classic treatise.

A. F.

Relativity. By F. W. LANCHESTER. (Constable. Pp. xiv and 222. Price 12s.)

Dr. Lanchester, as might have been predicted, has given us a lucid, stimulating, and thoroughly original book, which has its unorthodox moments.

Privileged, as he was, to hear the doctrines of Minkowski expounded, and to meet their author, as early as 1908, he was "one of the first, if not the first, Englishman to become inoculated with the new doctrines which for a long time attracted but little attention in this country." This circumstance has determined the outlook of the work, the first part of which, dealing mainly with the restricted theory, is in a direct line of development from Minkowski. The second part is concerned with gravitation—again a treatment based on Minkowski's work—the expanding universe, the principle of equivalence, and general space curvature.

Mathematics may be used as an instrument to save thought, and to grind out results by the mechanical following of a mechanical method. Dr. Lanchester's arguments are the complete antithesis of this. They involve only the simplest mathematics; they are thought-compelling and provocative, keeping the attention continually on the stretch; and the student of relativity mechanics, whatever view he may take of some of Dr. Lanchester's conclusions, will derive nothing but benefit from a critical perusal of the work.

A. F.

ERRATA IN VOL. XXXI.

Page 61 : In middle of long paragraph, for *Gegenionen* read *Nebenionen*.

Page 336, footnote 5, for *ssq.* read 559.

Page 340, 5th line, read SO_4 .

Page 343, top line, read *were* for *we* ; footnote 14, read *Hermann*.

Page 422 : See various contributions received whilst going to press.

Page 493. For $e - \frac{13,780}{RT}$ read $\exp\left(-\frac{13,780}{RT}\right)$.

Page 494. For $e - \frac{39,420}{RT}$ read $\exp\left(-\frac{39,420}{RT}\right)$.

Page 494. For $e - \frac{16,820}{RT}$ read $\exp\left(-\frac{16,820}{RT}\right)$.

Page 495. For $e - \frac{39,420}{RT}$ read $\exp\left(-\frac{39,420}{RT}\right)$.

Page 495. For $e - \frac{16,820}{RT}$ read $\exp\left(-\frac{16,820}{RT}\right)$.

Page 495. For $e - \frac{13,780}{RT}$ read $\exp\left(-\frac{13,780}{RT}\right)$.

Page 609. For last two lines read

$$L(\text{ZX}) = \gamma_{zx} + \delta_{zx} + \rho_{zx}. \quad L(\text{XY}) = \gamma_{xy} + \delta_{xy} + \rho_{xy}.$$

Page 610. For "Evaluation of $L(xy)$ and $L(zx)$ " read "Evaluation of $L(\text{XY})$ and $L(\text{ZX})$ ".

Page 610. For equation $\gamma_{zx} = -\frac{\epsilon\mu_{xy}}{(\text{XY} + \Delta)^2}$ read $\gamma_{zx} = -\frac{\epsilon\mu_{xy}}{(\text{ZX} + \Delta)^2}$.

Page 825. 15th line from top, for *qualitatively* read *quantitatively*.

Page 898. In Review of "Solid Geometry" by L. Lines, the name of the publishers should be Macmillan & Co.

Page 1220. Second paragraph, lines 6 to the end should be deleted and replaced by:—

annealed metal. This appears significant and suggests that interference with crystal growth, or inclusion of foreign matter, occurs under all conditions of deposition so far examined. It remains to be proved whether in soft deposits this hardening effect is entirely due to the presence of colloidal hydroxide in the film of liquid adjacent to the cathode, but if this is so, it may go far towards providing an explanation of the irreversibility of nickel deposition.

Page 1497. The mark † should be deleted from Table 3 ; the footnote † refers wholly to Table 4 on page 1500.

Page 1682. Fig. 10 : Curve C., The arrow should point to 60 (and not 70) R.H. For the same curve SO_2 was absent from 16 (and not 20) days.

Transactions of the Faraday Society.

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